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THE REACTIONS OF SULFUR ATOMS WITH OLEFINS

by



H. A. WIEBE

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES  
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September, 1967



THE UNIVERSITY OF ALBERTA  
FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled THE REACTIONS OF SULFUR ATOMS WITH OLEFINS submitted by H. A. Wiebe, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.



## ABSTRACT

The reactions of sulfur atoms have been examined with a series of hydrocarbon and fluorinated ethylenes. Statistical insertion of  $S(^1D)$  atoms into alkenyl C-H bonds gives rise to alkenyl mercaptans. Vinylic mercaptans are formed in reactions of  $S(^1D)$  atoms with olefins having an unsubstituted carbon atom and may arise by insertion into vinylic C-H bonds or isomerization of energized episulfide molecules. Episulfides result from addition to double bonds by either singlet or triplet state sulfur atoms.

The reaction of  $S(^3P)$  or  $S(^1D)$  atoms with cis and trans-1,2-difluoroethylene results in stereospecific addition to the double bond. Thus the criterion of stereospecificity for determining the spin-state of the reacting species cannot be applied to sulfur atom reactions with the double bond.

Carbon dioxide and carbon monoxide have been shown to be efficient electronic deactivators of  $S(^1D)$  atoms, while Xenon is ineffective in electronic deactivation.

The fluorinated ethylenes are less reactive than ethylene towards  $S(^3P)$  atom addition, resulting from a higher activation energy for the addition process to the fluorinated olefins. This is in agreement with the electrophilic character of sulfur atoms.





Attempts to formulate the structure of the activated complex for  $S(^3P)$  addition to double bonds is made by correlating reactivities with physical properties of the olefin. A correlation of reactivity with the ionization potential of the fluorinated olefins was not linear and may indicate that a charge transfer-complex is not the best description of the transition state. While a linear correlation was found with the atom localization energies of the olefins and may indicate a  $\sigma$ -complex structure for the transition state, stereospecificity of  $S(^3P)$  atom addition to the double bond indicates partial bonding to both carbon atoms.



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## CHAPTER I

### INTRODUCTION

Investigations concerning the chemical behavior of bivalent atoms have become increasingly important in the elucidation of the reaction mechanisms of bivalent chemical reagents in general. These species are characterized by similar electronic structure in that they have two unpaired interacting valence electrons, allowing for the possibility of at least two low lying electronic states with different multiplicities and energies. If the spin vectors of the electrons are antiparallel, the electronic state is designated a singlet; if the spins are parallel, a triplet state of three close-lying components results. Generally, in accordance with Hund's rule, the triplet state will be of lower energy and is referred to as the ground state.

The energy levels of low lying excited states of S, O, Se and C atoms are shown in Table I. Given the electronic configuration of these atoms there will be two possible excited singlet states. The small energy differences of the triplet components are usually not observable by chemical means and for convenience the ground state electronic configuration is simply designated as  $^3P$ .



TABLE I

ELECTRONIC LEVELS OF C, O, S AND Se ATOMS<sup>a</sup>

State	<u>Energy levels, kcal./mole</u>			
	C	O	S	Se
$3P_2$	0.06	0.00	0.00	0.00
$3P_1$	0.05	0.45	1.14	5.69
$3P_0$	0.00	0.65	1.64	7.25
$1D_2$	29.1	45.4	26.4	27.4
$1S_0$	61.9	96.6	63.4	64.2

<sup>a</sup> from reference (71)





The excited singlet states have long natural lifetimes with respect to radiative decay to the triplet ground state, since these transitions are spin forbidden. It is this feature that has created the great interest in biradical species, because it permits comparative studies of the chemical behavior of the excited singlet and ground state triplet species. The large amount of data accumulated for biradical species such as  $\text{CH}_2$ ,  $\text{NH}$ ,  $\text{S}$ ,  $\text{O}$ ,  $\text{C}$  and  $\text{Se}$  atoms show that not only reactivity but also the type of chemical reactions are affected by the spin state of the biradical. The pertinent features of the chemistry of these species will be reviewed in this context.

#### Reactions of Methylene

Many of the concepts relating the spin state of a biradical to a specified type of chemical reaction, such as insertion and addition, have originated from the studies of the chemistry of methylene. Several books and review articles (1,2,3,4,) include discussions on this topic and only the pertinent chemical evidence will be mentioned.

The most common sources of methylene have been the photolyses of ketene, diazomethane and diazirine. Herzberg (5,6) has obtained spectroscopic evidence that methylene from the photolysis of diazomethane is initially formed in a singlet state which then decays to the triplet. This provided the first evidence that the ground state of



methylene is a triplet. The energy difference separating the two states has as yet not been measured, but is believed to be small.

The most important reactions of methylene are insertion into C-H bonds and addition to carbon-carbon double bonds. The insertion reaction of  $\text{CH}_2$  into C-H bonds is quite general for a large variety of compounds. Meerwein, Rathjen and Werner (7) found the expected insertion products with diethyl ether, isopropyl alcohol and tetrahydrofuran. The indiscriminate nature of the insertion, with respect to primary, secondary and tertiary C-H attack, was first reported by Doering et al. (8) for n-pentane and 2,3-dimethylbutane in the liquid phase. Reactions of methylene with the  $\text{C}_7$ ,  $\text{C}_8$  and  $\text{C}_9$  alkanes in the liquid phase also showed random insertion into C-H bonds (9). The gas phase reactions are more selective, the insertion occurring preferentially in tertiary and secondary C-H bonds respectively. Frey and Kistiakowsky (10) found that the selectivity of insertion into secondary C-H bonds was 1.7 times that of primary bonds. Discrimination was further increased by the addition of inert gases.

Richardson et al. (9) suggested that the increased selectivity in the gas phase results from the reaction of triplet methylene which originate from the decay of the originally formed singlet. They proposed that in the liquid



phase, insertion of singlet methylene is much more rapid than relaxation to the triplet ground state. In the gas phase, the lower collision frequency allows deactivation of singlet methylene to the ground triplet state, followed by preferential H abstraction from the weaker secondary C-H bond and radical recombination, giving rise to "apparent" insertion products. At higher pressures more singlet state species will be reacting, and the reaction product ratios approach those observed in the liquid phase. Frey (11), through the use of  $O_2$  as a radical trap, estimated that 22% of the reaction between methylene and propane proceeds by initial hydrogen abstraction.

Gaspar and Hammond (12), on the other hand, suggested that the increased selectivity at low pressures results from the removal of excess vibrational and translational energy of the initially formed methylene before reaction. The "abstraction" was explained as fragmentation of energized insertion products and need not necessarily involve triplet methylene. Whatever the reason for the increase in discrimination, there is general agreement that singlet methylene inserts into C-H bonds and the triplet undergoes a hydrogen abstraction reaction.





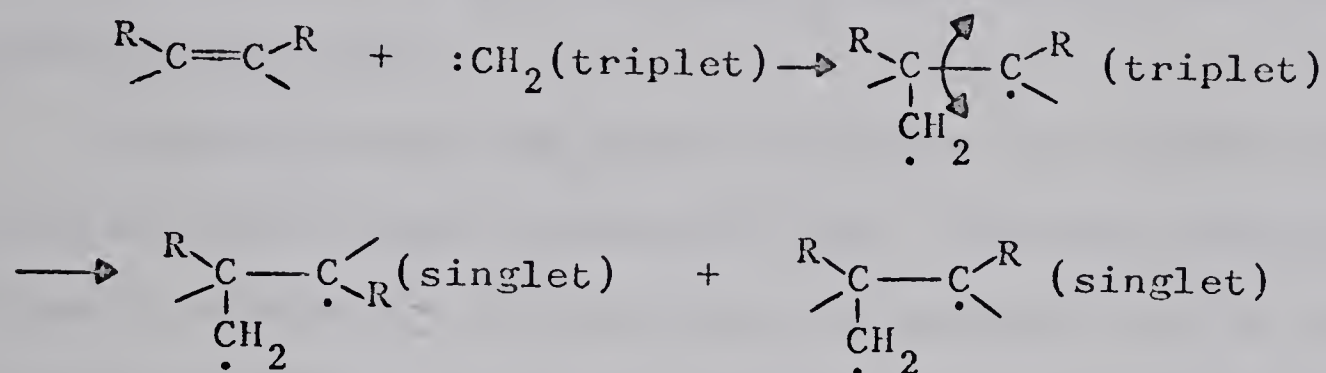
Methylene reacts with olefins by insertion into alkyl and vinylic C-H bonds and by addition to double bonds to form cyclopropanes. Thus the products from the propylene reaction were methylcyclopropane and the four isomeric butenes (14). The isobutylene reaction gave 1,1-dimethylcyclopropane, 2-methylbutene-1 and 2-methylbutene-2 (15). The reaction with the C-H bonds was 10-20 times slower (depending on the source of methylene) than the reaction with the double bond. Methylene produced by diazomethane photolysis was less discriminate in its reactions with C-H and double bonds than was methylene from ketene photolysis (15). This was attributed to excess translational energy carried by methylene in the former case, since the addition of inert gas to the diazomethane system resulted in the same product ratios as in the ketene system.

In reactions with olefins, the differences in chemical characteristics of singlet and triplet methylene are best exemplified by the addition reaction with the double bond. An early suggestion by Skell and Woodward (16) that stereospecificity of addition is a criterion for the spin state of the attacking methylene has led to a number of investigations which are in agreement with this proposal. They reasoned that singlet methylene adds to a double bond in a single concerted step, and being spin allowed, results in the retention of geometric configuration in the parent molecule.





Triplet addition involves the formation of a triplet biradical and rapid rotation, compared to spin inversion, in the intermediate would destroy the original configuration of the olefin:



Methylene, from the photolysis of diazomethane in gas or liquid phase, adds stereospecifically to both trans and cis-2-butene (16,17,18,19). Addition of inert gases (20, 21,22) or production of triplet methylene by mercury (23) or benzophenone sensitization (24) of ketene leads to non-stereospecific addition to cis-2-butene.

Benson and DeMore (3) suggested that a biradical is initially formed in both singlet and triplet methylene addition to the double bond. The kinetic parameters for rotation and cyclization will then determine whether or not configuration will be retained in the products. Addition of triplet methylene to ethylene results in a trimethylene biradical containing 32.7 kcal./mole excess energy and it was calculated that ring closure should be  $10^{0.8}$  times faster than rotation. Singlet methylene addition should result in even faster ring closure, since the excess energy in the biradical would be greater.

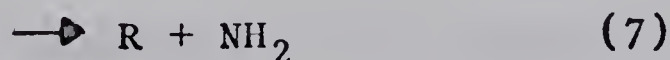
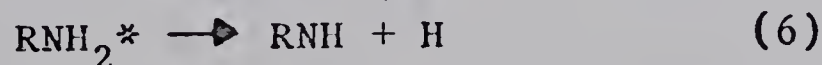
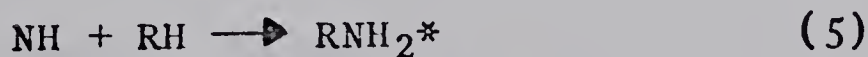
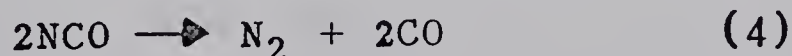
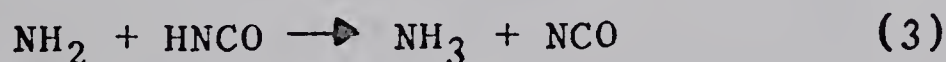
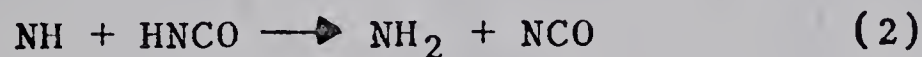


### Reactions of NH

The chemical behavior of the NH radical is expected to be similar to that of isoelectronic methylene. Two low lying singlet states are possible for NH,  $^1\Delta$  and  $^1\Sigma^+$ , having energies of 27 and 55 kcal./mole respectively above the  $^3\Sigma^-$  ground state (25).

Hydrogen azide ( $\text{HN}_3$ ) and isocyanic acid ( $\text{HNCO}$ ) have been the most common sources for NH. From the limited kinetic studies of this species, it appears that NH also undergoes addition to double bonds as well as abstraction and insertion reactions with C-H bonds. Attempts, however, to isolate such reaction products in the gas phase have for the most part been unsuccessful.

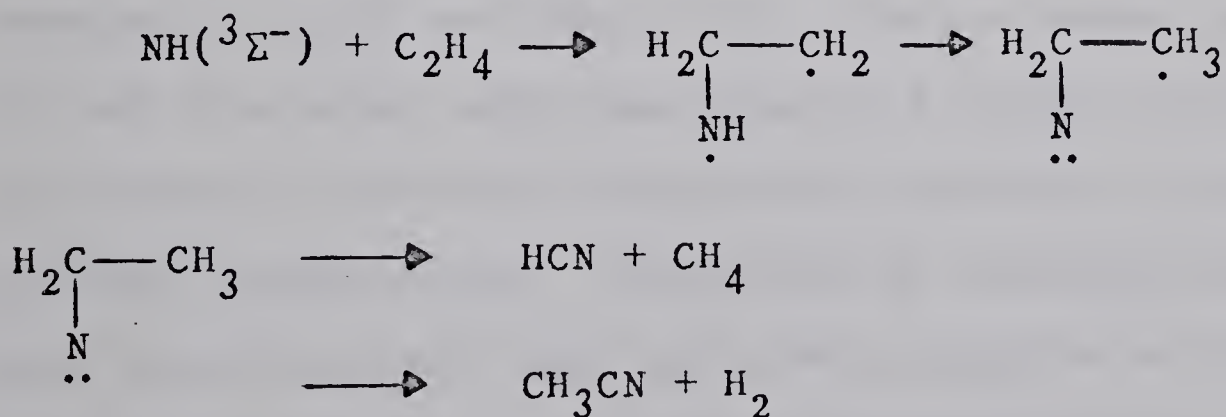
Back et al. (26,27) have investigated the reactions of NH with paraffins and olefins in the gas phase.  $\text{HNCO}$  was used as the source of NH and they postulated the following scheme for the reaction:





No amines or other nitrogen-bearing compounds were found with either paraffins or olefins. It was assumed that these are formed in a vibrationally excited state and are lost by decomposition as indicated by reactions 5-8, or in the case of the olefin reaction through rearrangement and polymerization. However, upon addition of a hydrocarbon to HNC0 the yield of CO falls to about 1/3 of the value obtained from the photolysis of HNC0 alone. This indicates that all the NH radicals produced in step 1 are scavenged. The only volatile product from the HNC0-propane system was 2,3-dimethylbutane, indicating that reaction 8 occurs at the weaker secondary C-H site.

Cornell et al. (28) have recently shown that the reaction of NH, from HN<sub>3</sub>, with ethylene results in the formation of HCN, CH<sub>3</sub>CN, CH<sub>4</sub>, H<sub>2</sub> and an amorphous solid. The exclusive reactive species was shown to be ground state NH radicals. The suggested mechanism was:



This hypothesis was supported by the photolysis of ethyl azide which produces the same C<sub>2</sub>H<sub>5</sub>-N: transient. The





products in the gas phase were the same as for the NH-ethylene system.

Jacox and Milligan (29) obtained ethylene imine as a product from the photolysis of  $\text{HN}_3$  and ethylene in a solid argon matrix at  $4^\circ \text{K}$ . In the reaction with acetylene, keteneimine may have been formed by the addition of NH in an analogous reaction:



Miller (30) has investigated the reactions of the NH radical, from  $\text{NH}_3$ , with a number of paraffins at room temperature. In the gas phase appreciable attack of the NH radical on paraffins larger than  $\text{C}_2$ , leads to the formation of amines. Insertion into C-H bonds was suggested as a possible mechanism for the formation of the amines.

#### Carbon Atom Reactions

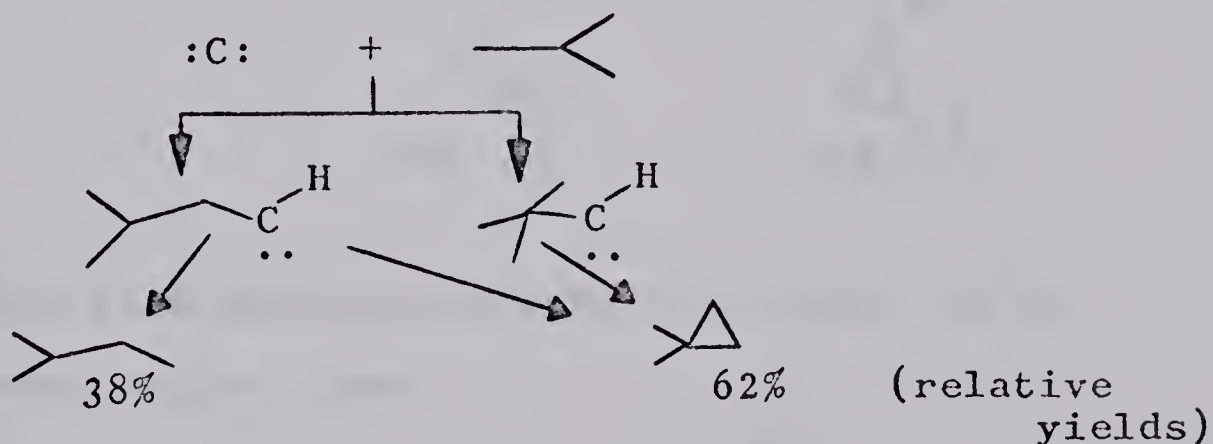
The chemical behavior of carbon atoms has recently been studied by Skell and Engel (31). Carbon atoms, in the  $^1\text{S}$ ,  $^1\text{D}$  and  $^3\text{P}$  states, were generated by a carbon arc and deposited in paraffinic hydrocarbon matrices at liquid nitrogen temperatures. Deposition of reactants could be made simultaneously with the carbon vapor or at a later time. This enabled Skell and Engel to measure the lifetimes of the two metastable states by the chemical analysis of products. The half-life of  $\text{C}(^1\text{S})$  was estimated to be 2 seconds and





that of  $C(^1D)$  15 seconds. The time delay technique also permitted the elucidation of the reactions associated with each electronic state.

Reactions with paraffins were only observed if the carbon vapor and reactant were deposited simultaneously. This suggested that all products result from reactions of the  $^1S$  state of carbon. Isobutane yielded 1,1-dimethylcyclopropane and 2-methylbutane as the major products. The initial reaction was postulated to be an insertion into either a primary or tertiary C-H bond giving rise to free intermediate carbenes:

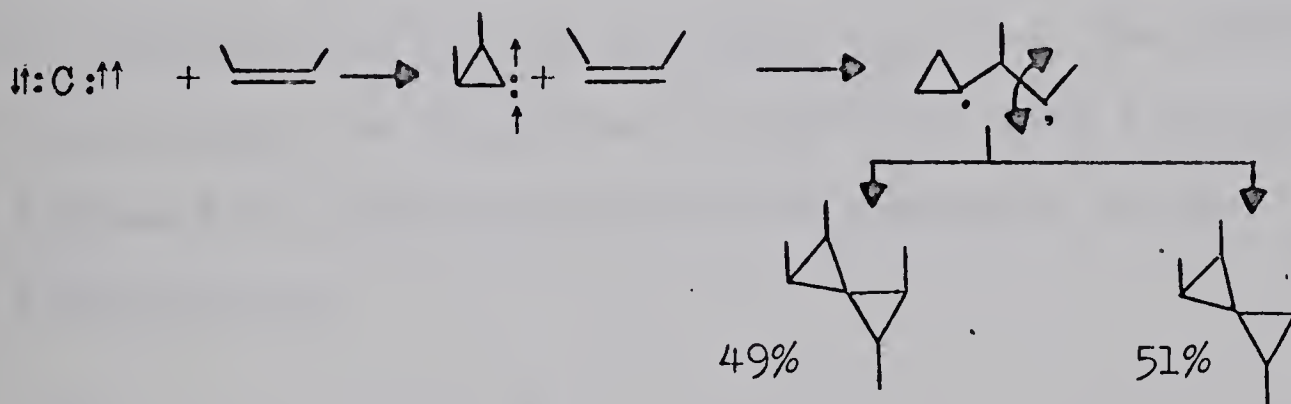


Both carbenes can undergo intramolecular insertion to give 1,1-dimethylcyclopropane. The isobutyl carbene can abstract hydrogen from surrounding isobutane molecules to produce 2-methylbutane since isomeric octanes resulting from radical coupling were observed. Neither 2-methylpropene nor acetylene were observed. Cyclopropane and carbon atom reactions gave methylene cyclopropane as the

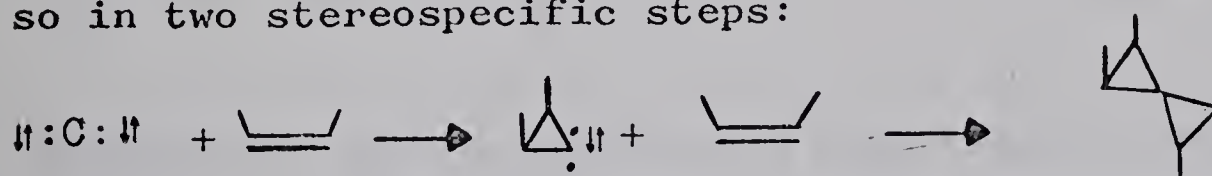


major product. Isomeric  $C_6$  materials, from radical coupling reactions, were present but again no acetylene was found.

Triplet ground state carbon atoms were shown to react with cis and trans-2-butene forming substituted spiropentanes as the only products. The isomeric distribution of products indicated that the addition mechanism is comprised of one stereospecific and one non-stereospecific process:



$C(^1D)$  atoms also form spiropentanes with olefins, but do so in two stereospecific steps:



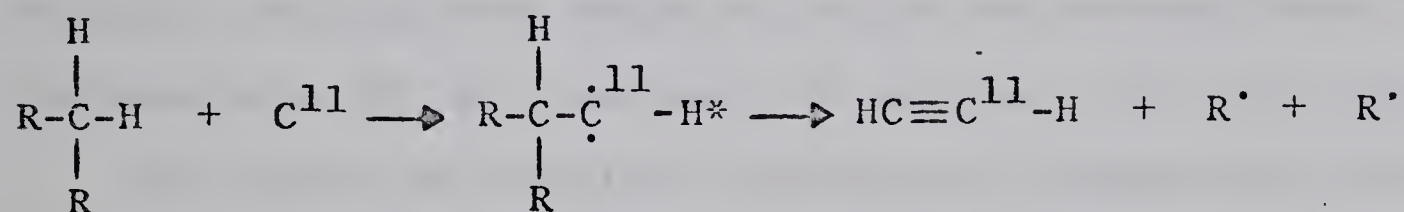
$C(^1S)$  atoms reacted with cis-2-butene to give 1,3-dimethylallene and possibly spiropentanes.

MacKay and Wolfgang (32) employed a different technique for generating carbon atoms in their studies of the reactions with hydrocarbons.  $C^{11}$  atoms were produced in situ by the  $C^{12}(\gamma, n)C^{11}$  nuclear reaction or by stripping neutrons from an



external beam of 120 Mev ions, in which case the atoms entered the reaction vessel through a brass foil. It was suggested that  $C^{11}$  atoms from the latter process are in the ground  $^3P$  state at the time of reaction. The carbon atoms formed by these methods will have high kinetic energies and must be moderated before they can react as neutral atoms.

A high yield of acetylene was always obtained in reactions of  $C^{11}$  atoms with paraffins and olefins (33,34,35). To explain this for the paraffin reaction, the initial interaction was described as insertion into a C-H bond, followed by decomposition of the energized carbene intermediate:

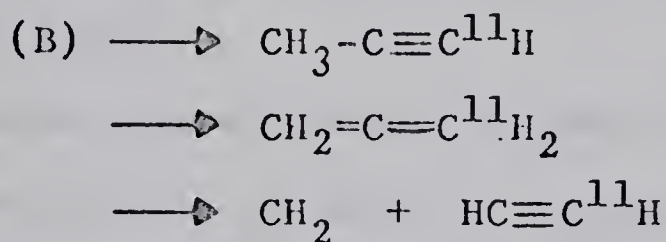
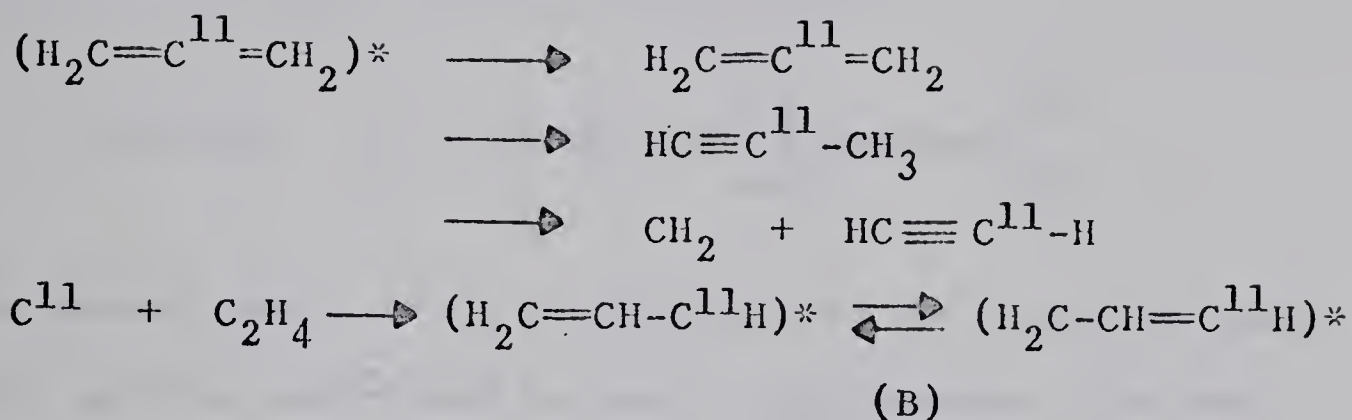
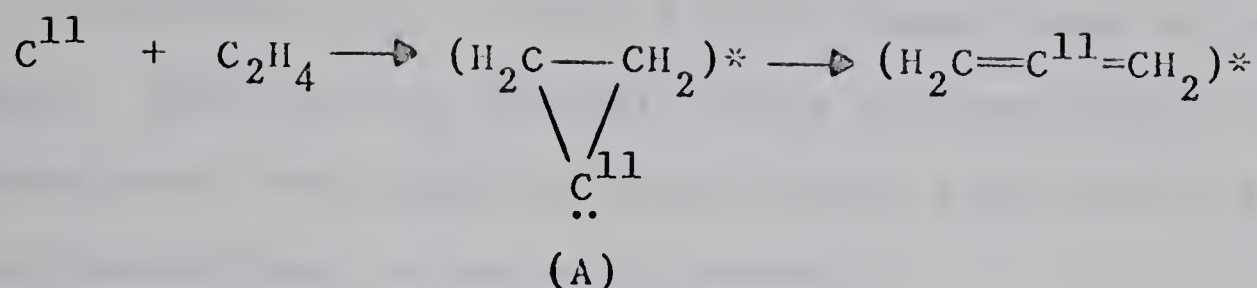


Products in smaller yield were explained in terms of a more complex rearrangement of the intermediate carbene. Thus in the reaction with propane, sufficient energy was available to yield ethylene, propylene, allene, methylacetylene and butadiene.

In reactions with olefins,  $C^{11}$  atoms underwent double bond addition as well as C-H insertion (34,35). The reaction with ethylene was represented by the following scheme:







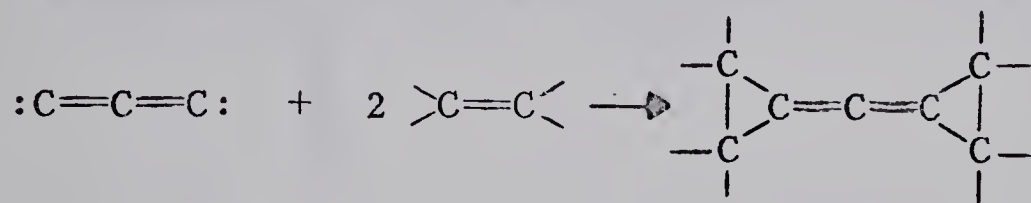
Products arising from addition of the cyclopropylidene intermediate (A) to a molecule of ethylene were not observed.

The yield of acetylene was greatly reduced when the reaction was carried out in inert gas matrices (36), but contrary to Skell's results no spiropentane was formed. Apparently the chemical potential and reactivity of translationally "hot" carbon atoms is so high, that even in the solid phase energized reaction intermediates are formed. The added kinetic energy also probably makes reactions of carbon atoms much less discriminate with respect to the mode by which it becomes chemically combined. This may account for the differences in results obtained from the two sources of carbon atoms.





Dicarbene,  $C_3$ , is also a major constituent of carbon vapor. Skell et al. (37,38), using the previously mentioned techniques, have reported that olefins react with  $C_3$  to form bisethanoallenes as the only products:



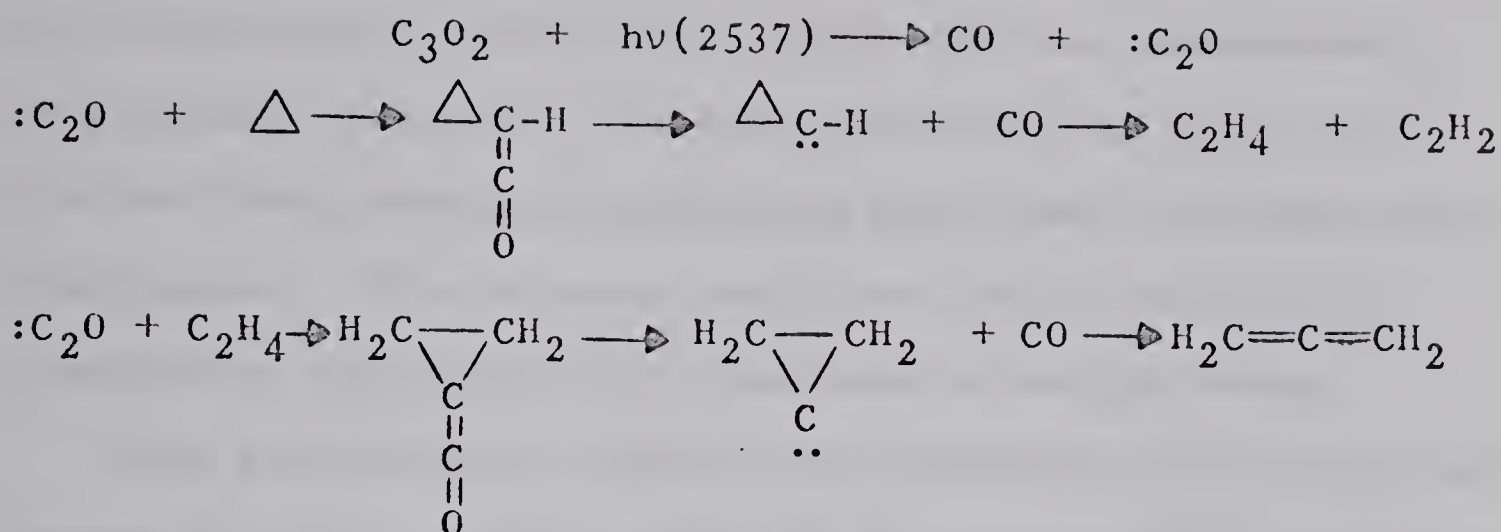
The ground state of  $C_3$  is believed to be a singlet and this species was found to add to cis-butene-2 in two stereospecific steps.

Simultaneous deposition of  $C_3$  and olefin on the hydrocarbon matrix led to product formation that suggested one stereospecific and one non-stereospecific step for the addition processes. This was attributed to reaction of an excited triplet state of  $C_3$ .

Photolysis of carbon suboxide in the presence of methane at  $1470 \text{ \AA}$  (39) indicates that carbon atoms are also formed in this system. Acetylene and ethylene were formed as major products. At  $2537 \text{ \AA}$ , ethylene was the only product (40) and may indicate that  $:C_2O$  is the reactive species in the longer wavelength photolysis, since secondary photolysis of ethylene to form acetylene at the shorter wavelength was shown to be negligible (38,41).

$C_2O$  also reacts with cyclopropane and ethylene (40,42, 43) to yield products that suggest insertion into C-H bonds and addition to double bonds:





Mullen and Wolf (44) photolyzed carbon-2- $\text{C}^{14}$ -suboxide in ethylene and found the isotopic distribution in the product allene to be 92%  $\text{C}^{14}$  in the central carbon position. This suggested that allene was formed mainly by addition to the double bond and not insertion into the C-H bond.

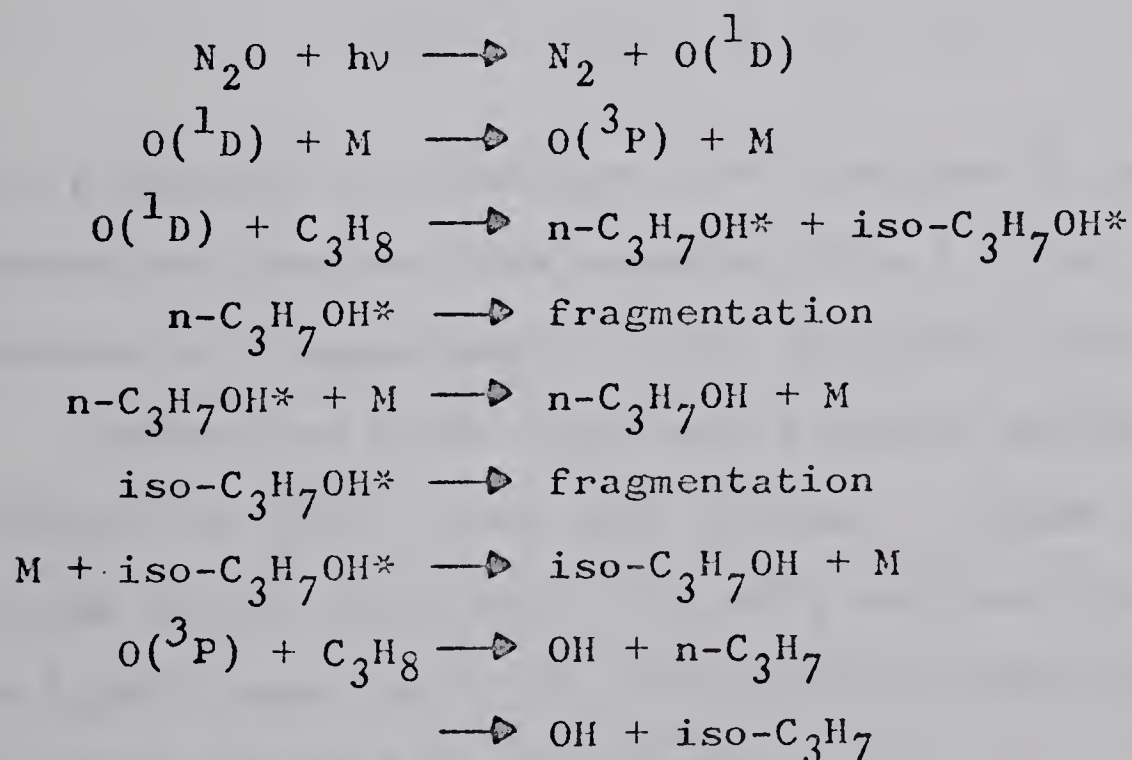
### Reactions of Oxygen Atoms

Three commonly used methods for generating oxygen atoms are: (a) the electrode discharge of  $\text{O}_2$  or  $\text{H}_2\text{O}$  in a flow system; (b) photolysis or mercury sensitization of  $\text{N}_2\text{O}$ ,  $\text{NO}_2$  or  $\text{O}_3$ ; and (c) titration techniques in which atomic oxygen is formed through the reaction  $\text{N} + \text{NO} \longrightarrow \text{N}_2 + \text{O}$ , achieved by injecting nitric oxide into a stream of active nitrogen. The electrode discharge has been used extensively by Avramenko (45) to study reactions of oxygen atoms with paraffins and olefins. It has proved disadvantageous in that the primary products of the reaction undergo extensive fragmentation at the low pressures used in the flow system. Hence



the reactions involved must be deduced from measurements of secondary products. Further complications arise from the fact that products containing more than one oxygen atom also appear. This in many cases has led to incorrect conclusions concerning the reactions of oxygen atoms.

The photochemical method for production of O atoms has proved the most useful source for elucidating the reactions of oxygen atoms. Direct photolysis of nitrous oxide was used by Yamazaki and Cvetanovic (46) to produce  $O(^1D)$  atoms. In the  $N_2O$  - propane system three major processes were shown to be operative: (a) random insertion of  $O(^1D)$  atoms into C-H bonds; (b) deactivation, followed by abstraction of hydrogen by  $O(^3P)$  atoms; and (c) pressure-dependent fragmentation of the energized insertion products:

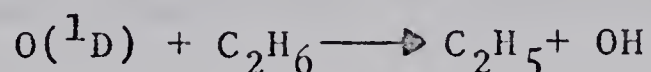






When inert gases capable of electronically deactivating excited oxygen atoms were added, the insertion and fragmentation decreased and the abstractive processes at the secondary C-H sites became more extensive. From the increased selectivity of abstraction, the following relative deactivating efficiencies of different gases were obtained: Xe=0.47, N<sub>2</sub>=0.15, Kr=0.05 with He and SF<sub>6</sub> being close to zero.

Previous investigations of the O(<sup>1</sup>D)-ethane system, using direct photolysis of nitrous oxide as the source of oxygen atoms, showed ethyl alcohol to be a major product (47,48). Its formation could be completely suppressed by the addition of iodine as a scavenger. Hence it was suggested that the initial process was a hydrogen abstraction:

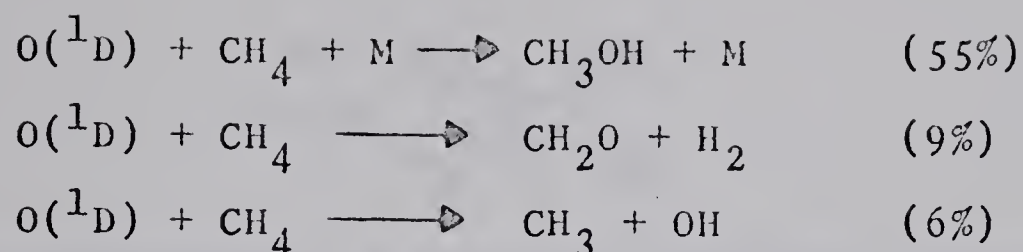


Low pressures of substrates were used and it could not be determined whether this resulted from a direct "stripping" process or fragmentation of the energized insertion product.

DeMore and Raper (95) have recently studied the reaction of O(<sup>1</sup>D) atoms with methane. Oxygen atoms were obtained by the 2537 Å photolysis of <sup>o</sup>O<sub>3</sub>-CH<sub>4</sub> mixtures dissolved in liquid argon at 87 °K. The results indicated that the reaction proceeds by three paths:



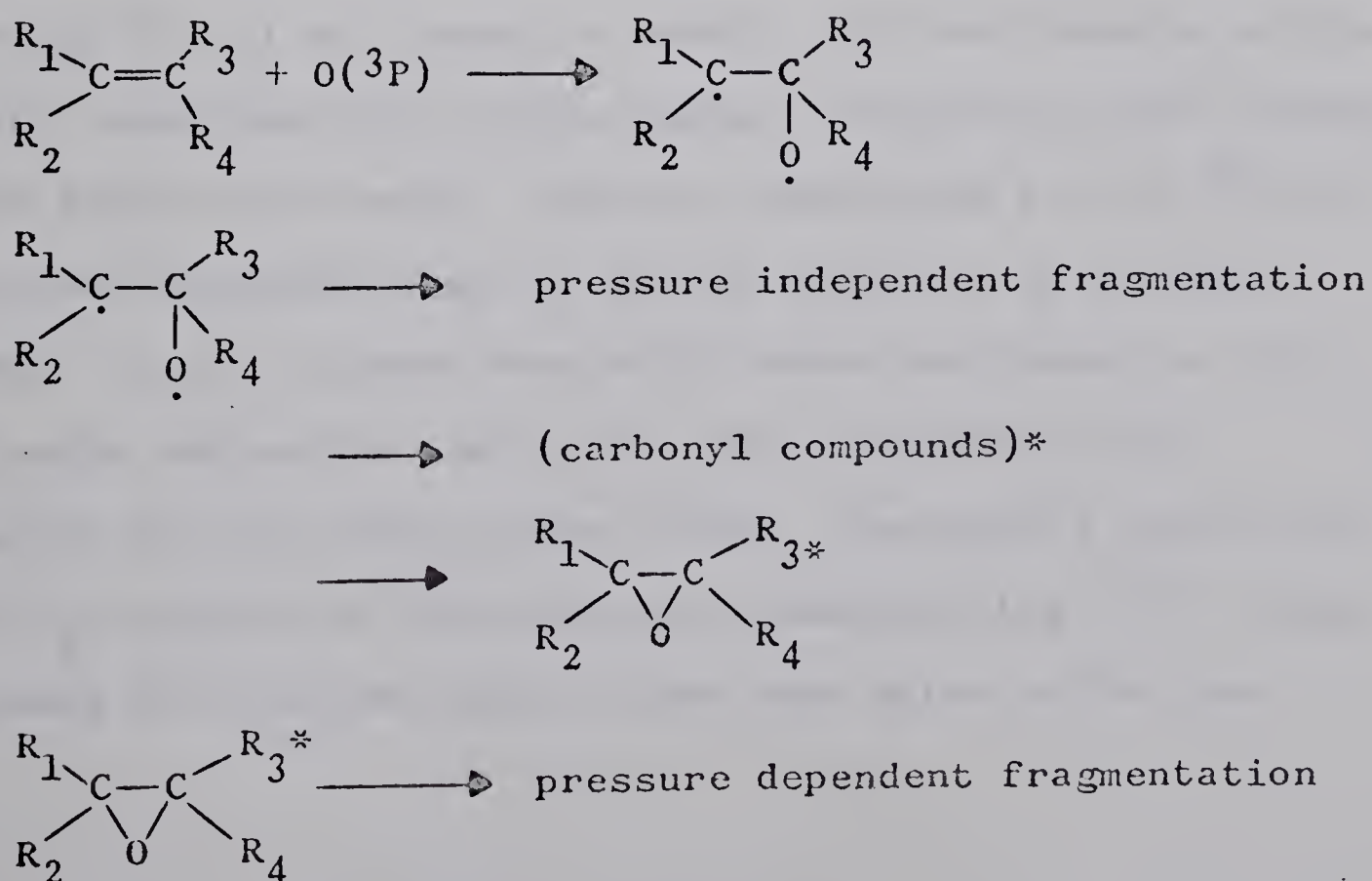




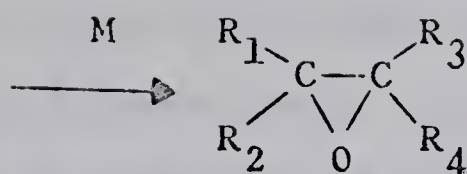
The remaining 30% of the  $\text{O}(^1\text{D})$  atoms were deactivated by  $\text{CH}_4$  to the ground triplet state.

Cvetanovic has recently reviewed the reactions of triplet oxygen atoms with olefins (49). Cvetanovic used mainly photochemical means for the generation of  $\text{O}(^3\text{P})$  atoms, such as the mercury sensitization of nitrous oxide or direct photolysis of  $\text{NO}_2$  in the wavelength region 2537-4040 Å.

It was postulated that the initial interaction with the double bond leads to the formation of a triplet biradical, in agreement with spin conservation rules, followed by rearrangement and fragmentation (50,51,52):







(carbonyl compounds)\*  $\longrightarrow$  pressure dependent fragmentation



From product compositions and pressure effects the following conclusions have been drawn:

- (1) Addition of  $\text{O}(^3\text{P})$  atoms to the double bond is non-stereospecific. This was shown by the addition reaction to cis or trans-2-butene; mixtures of cis and trans-2-butene oxide are formed with either olefin.
- (2) The oxygen atom preferentially adds to the least substituted carbon atom.
- (3) Internal rearrangements of the initial biradical lead to aldehyde and ketone formation.

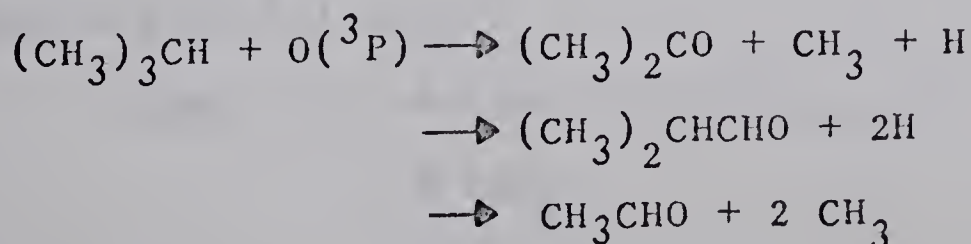
Photolysis of  $\text{NO}_2$ -1-butene mixtures in the wavelength region 4047-2537 Å ( $^1\text{O}$  (53)) was found to exhibit all the features of the mercury sensitized  $\text{N}_2\text{O}$ -olefin systems, indicating that triplet oxygen atoms are formed. However, photolysis at 2288 Å ( $^1\text{O}$  (54)) led to an increased yield of epoxide relative to n-butyraldehyde. It was assumed that  $\text{O}(^1\text{D})$  atoms are formed at this wavelength and add to the double bond by simultaneous formation of two carbon-oxygen bonds. Increasing amounts of added  $\text{N}_2$ , capable of electronically deactivating  $\text{O}(^1\text{D})$  atoms, decreased the epoxide yield to the same value as for the



longer wavelength photolysis, indicating that  $O(^1D)$  atoms are formed by 2288 Å photolysis. Attempts to verify the stereospecificity of addition of  $O(^1D)$  atoms by the use of cis and trans-2-butene were inconclusive, being complicated by a secondary reaction of the β-butene oxides with  $NO_2$ . Products indicating insertion into methyl groups of the olefin were absent, but they may also have been lost through a reaction with  $NO_2$ .

Recent observations (97) of the reactions of  $O(^1D)$  atoms, from the photolysis of  $N_2O$ , with trans-2-butene in the liquid phase have shown that the addition reaction is stereospecific. The formation of trans-2-buten-1-ol indicates that insertion into C-H bonds of the methyl groups also occurs.

Woods et al. (55) have shown that the primary step in the reaction of  $O(^3P)$  atoms, from the mercury sensitization of  $N_2O$ , with isobutane is hydrogen abstraction, preferentially at the tertiary C-H site. Wright (107), on the other hand, using the titration technique to produce triplet oxygen atoms, suggested that the main reaction involved alkyl and hydrogen displacement, with hydrogen abstraction being of minor importance.







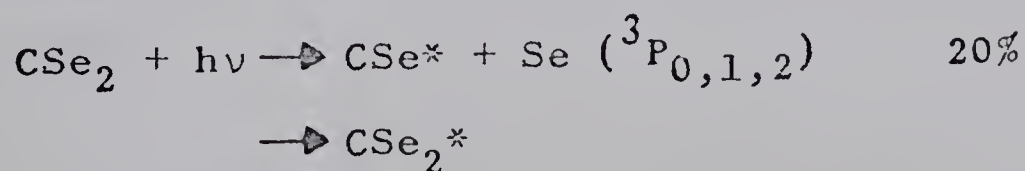
The relative rates of addition of  $O(^3P)$  atoms to a series of olefins (56,57) showed that triplet oxygen atoms have a definite electrophilic character. The pre-exponential factors for the addition reaction were found to be constant and variations in reactivity depended upon activation energy differences.

#### Reactions of Selenium Atoms

Callear and Tyerman have shown that  $Se(^1D)$  and  $Se(^3P)$  atoms react with olefins to form cyclic selenides (58,59). Selenium atoms were shown to be formed in the flash photolysis of carbon diselenide and oxyselenide (58,59). The former yielded triplet state atoms, while the latter resulted in singlet state species. When olefins were added to the system, new bands appeared in the absorption spectrum which have been tentatively assigned to the cyclic selenides. The selenides were found to be unstable and decomposed within a few minutes.

$Se(^1D)$  atoms from the photolysis of  $COSe$  in a static system, have been shown to insert into C-H bonds of paraffins to form selenomercaptans (60).

The relative rates of addition of  $Se(^3P)$  atoms to olefins have also been reported by Callear and Tyerman (61). Isothermal flash photolysis of carbon diselenide was employed to generate  $Se(^3P)$  atoms:







Nitrogen was used to deactivate any excited atoms to the Boltzman distribution of the triplet components. The formation of cyclic selenides was monitored by absorption spectroscopy using the ethylene selenide bands as a standard. Activation energies and Arrhenius parameters were obtained and indicated that reactivity is related only to the activation energy of addition. The results in Table II show that ground state group VI atoms Se, O and S, and to a lesser extent triplet methylene, exhibit similar electrophilic character.

#### Reactions of Sulfur Atoms

The reactions of sulfur atoms with paraffins and olefins have recently been investigated (62,63,64,65). The photolysis of carbonyl sulfide provided a clean source of sulfur atoms for these systems. The UV absorption spectrum of COS consists of a banded spectrum extending from about 2600 to 1800 Å, with a maximum at 2235 Å. The first excited state of COS has a radiative lifetime of about  $10^{-9}$  sec. (calculated from the integrated absorption coefficient), and semi-empirical M.O. calculations indicate that the transition is of the  $\pi-\pi^*$  type (66). The heat of formation of ground state sulfur atoms is 66.0 kcal./mole (67) and that of COS is -32.8 kcal./mole (68). It then follows that  $D(OC=S) = 72.4$  kcal./mole



TABLE II

RELATIVE RATES OF ADDITION OF  $\text{CH}_2(^3\Sigma)$ ,  $\text{S}(^3\text{P})$ ,  $\text{O}(^3\text{P})$   
 AND  $\text{Se}(^3\text{P})$  ATOMS TO OLEFINS

Olefin	$\text{O}(^3\text{P})^a$	$\text{Se}(^3\text{P})^b$	$\text{S}(^3\text{P})^c$	$\text{CH}_2(^3\Sigma)^d$
ethylene	1.00	1.00	1.00	1.00
propylene	5.75	2.6	6.9	1.0
<u>trans</u> -2-butene	28.3	56	20	0.89
<u>cis</u> -2-butene	23.8	23.9	16	0.94
1-butene	5.75	7.1	10	1.6
isobutylene	15.0	44.7	50	2.9
1-pentene	-	5.0	10	-
2-methyl-1-butene	-	-	56	-
cyclopentene	29.8	-	18	-

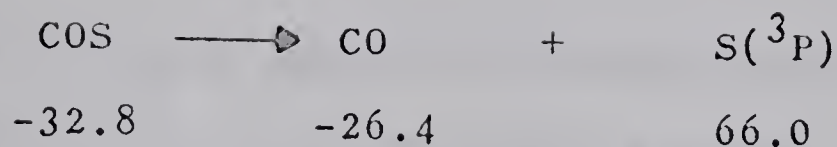
<sup>a</sup> from reference (49)

<sup>b</sup> from reference (61)

<sup>c</sup> from reference (70)

<sup>d</sup> from reference (96)





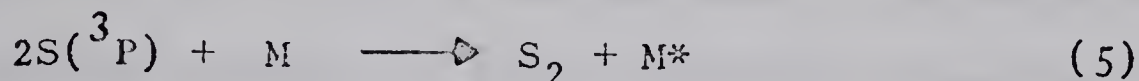
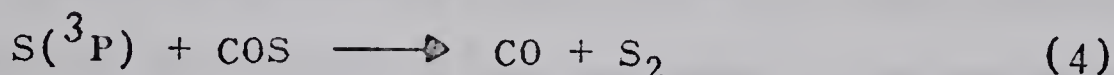
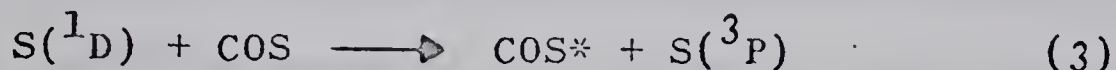
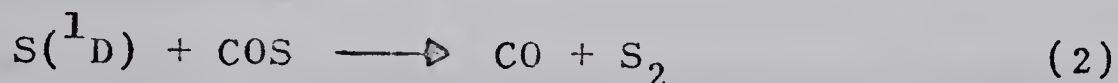
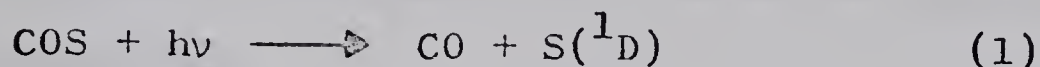
and the spin allowed dissociation



will require 98.8 kcal./mole corresponding to  $\lambda$  2895 Å.

To produce S atoms in the  $^1\text{S}$  state requires 135.8 kcal./mole corresponding to  $\lambda$  2105 Å.

The proposed scheme for COS photolysis was (66):



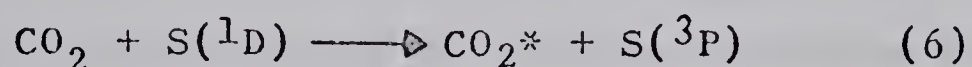
The measured quantum yield for CO formation was 1.8 at 2537 Å, suggesting that 5 is of minor importance. Radiative or non-radiative decay of the excited state would also account for a quantum yield of less than two, if step 5 is not operative.

Alkyl mercaptans were formed when COS was photolyzed in the presence of paraffins. Isomeric mercaptans were obtained from propane and isobutane in a statistical ratio indicating indiscriminate attack on the C-H bonds. Cyclopropane gave only cyclopropane mercaptan; no isomerization to allyl mercaptan occurred. Methane was the only paraffin to yield additional products that indicated decomposition of energized mercaptan molecules.



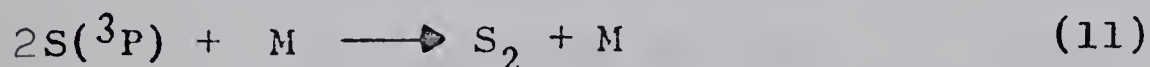
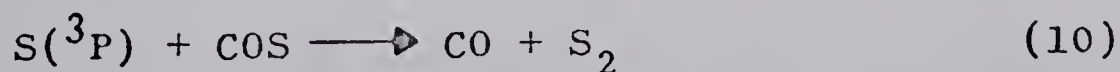
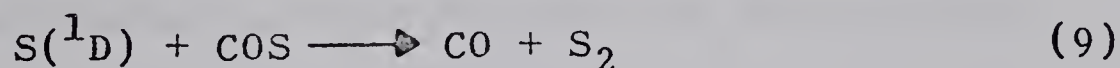
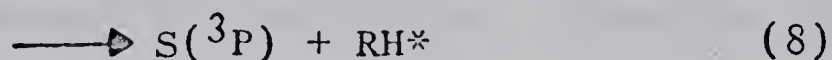
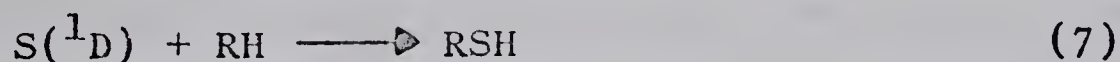


Addition of  $\text{CO}_2$  to paraffin systems resulted in complete suppression of the mercaptan products. This was interpreted as proof that  $\text{S}(^1\text{D})$  atoms are the species undergoing insertion, since  $\text{CO}_2$  should be an efficient collisional deactivator of singlet atoms:



Hence, as for singlet methylene and oxygen atoms,  $\text{S}(^1\text{D})$  atoms are capable of non-selective insertion into C-H bonds of paraffins.

The alkyl mercaptans were formed in increasing yield as the paraffin pressure was increased and a simultaneous decrease in CO formation was observed. The rates of formation became constant at higher paraffin pressures, with  $\text{R}(\text{CO})$  being greater than half the rate obtained with pure COS. A reaction scheme was then suggested as follows:



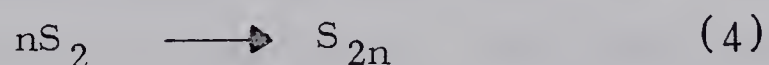
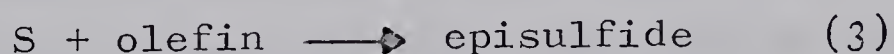
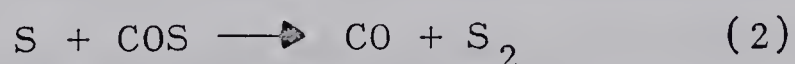
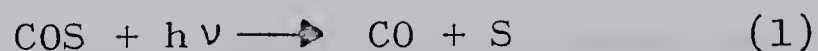
A stationary state treatment of the scheme gave the following relation:



$$\frac{R^O(CO)}{2} \cdot \frac{P(RH)}{R(RSH)} = \frac{k_9}{k_7} \cdot \frac{P(COS)}{k_7} + \frac{k_7 + k_8}{k_7} \cdot \frac{P(RH)}{k_7} \quad I$$

Plots of equation I for a series of open-chain and cyclic paraffins were linear, with identical slopes and intercepts. The relative rate constant values were  $k_9/k_7 = 2.0$  and  $k_8/k_7 = 0.70$  for photolysis by a filtered medium pressure Hg-arc ( $2490 \text{ \AA}$ ). The ratio  $k_8/k_7$  decreased to 0.3 in photolyses using a Cd resonance lamp ( $2288 \text{ \AA}$ ), indicating an increase in the rate of the insertion reaction. This was attributed to excess translational energy carried by the sulfur atom in photolyses at  $2288 \text{ \AA}$ .

The olefin-sulfur atom reaction has been examined with ethylene and propylene (62). The brief investigation, employing only a gas burette and mass spectrometry for analysis indicated that episulfides (cyclic sulfides) were the only products formed. At high olefin pressures  $R(CO)$  approached that of  $R^O(CO)/2$ , indicating that all the sulfur atoms from reaction 1 are scavenged by the olefin. Therefore the following mechanism was proposed for the reaction:





A stationary-state treatment of the reaction steps gave the following expression:

$$\frac{1}{R(\text{CO}) - R^0(\text{CO})/2} = \frac{P(\text{olefin})}{k R^0(\text{CO})/2} + \frac{2}{R^0(\text{CO})}$$

where  $k = k_2 P(\text{COS})/k_3$ . However,  $k$  was found to be pressure-dependent. This was attributed to deactivation of  $S(^1\text{D})$  atoms by the olefin, by analogy with the COS-paraffin system:



and results in an additional episulfide-forming reaction.

Reactions of  $S(^1\text{D})$  atoms with the four isomeric butenes (69) showed that in addition to episulfides, alkenyl mercaptans are also formed. Triplet state sulfur atoms were found to add stereospecifically to cis and trans-2-butene and, therefore, invalidate the criterion of stereospecificity as related to the spin state of the adding species for sulfur atom addition.

### The Present Investigation

The formation of alkenyl mercaptans in the COS-C<sub>4</sub>-olefin systems showed that singlet sulfur atoms undergo insertion reactions with alkenyl C-H bonds. A similar reaction with vinylic C-H bonds should result in the formation of vinylic mercaptans. Although vinylic mercaptans are known to be relatively unstable compounds (81), they may be formed in sufficient quantities for detection. For this reason the ethylene, propylene, 1-butene and isobutylene systems are re-examined. To determine whether the sulfur atom reaction





is general for other olefins, a series of fluorinated ethylene systems are investigated.

The reaction of  $S(^3P)$  atoms with the 2-butenes has resulted in stereospecific addition to the double bond. To determine if the addition process is stereospecific for other geometric isomers, the reactions of  $S(^3P)$  atoms with cis and trans-1,2-difluoroethylene are examined. Addition of carbon dioxide to COS-olefin systems is employed to investigate the triplet state sulfur atom reactions, since  $CO_2$  has been shown to be an efficient deactivator of  $S(^1D)$  atoms.

The effect of added Xe and CO on the  $COS-C_2H_4$  system is investigated to determine if other gases are capable of electronically deactivating  $S(^1D)$  atoms.

In the paraffin-COS systems, an increase in the energy of the exciting radiation has resulted in a faster rate for the insertion reaction. This was attributed to excess translational energy carried by the sulfur atom at higher energy photolyses. Photolyses of COS-olefin systems at 2490, 2288 and 2139 Å are carried out to see if a similar effect is observed in the olefin reaction.

The effect of temperature on COS-olefin systems is examined to determine the activation energy differences of the episulfide- and mercaptan-forming steps. The reaction of sulfur atoms is studied with  $C_2D_4$  to determine whether isotope effects are present.

The electrophilic character of  $S(^3P)$  atoms has been





shown by the relative rates of  $S(^3P)$  atom addition to a series of hydrocarbon olefins. To determine the effect electron withdrawing groups would have on the reactivity of  $S(^3P)$  atoms with the double bond, three fluorinated ethylene systems are investigated.



## CHAPTER II

### EXPERIMENTAL

#### 1) The high-vacuum system

The high-vacuum apparatus employed was constructed of Pyrex tubing in the usual fashion. Fig. 1 illustrates the locations of the photolytic assembly, distillation train, storage system and Toepler pump-gas burette arrangement. Delmar mercury float valves and Hoke helium-tested valves were used throughout to prevent the loss of products in stopcock grease. The pumping system consisted of a two-stage mercury diffusion pump backed by a Welch duoseal oil pump. A McLeod gauge was used to measure pressures less than one torr and calibrate the Pirani gauge tubes (Consolidated Electrodynamics Cat. No. GP-001). These were used to monitor distillations and gas transferences.

#### 2) Photolytic assembly

A cylindrical quartz cell, 100 mm. in length and 50 mm. in diameter, was used as a reaction vessel in the static system. A graded quartz-to-pyrex seal attached to a Hoke, Model TY440, valve connected the cell to the high-vacuum system. The reaction cell and lamp were kept in constant positions by 3-pronged clamps.



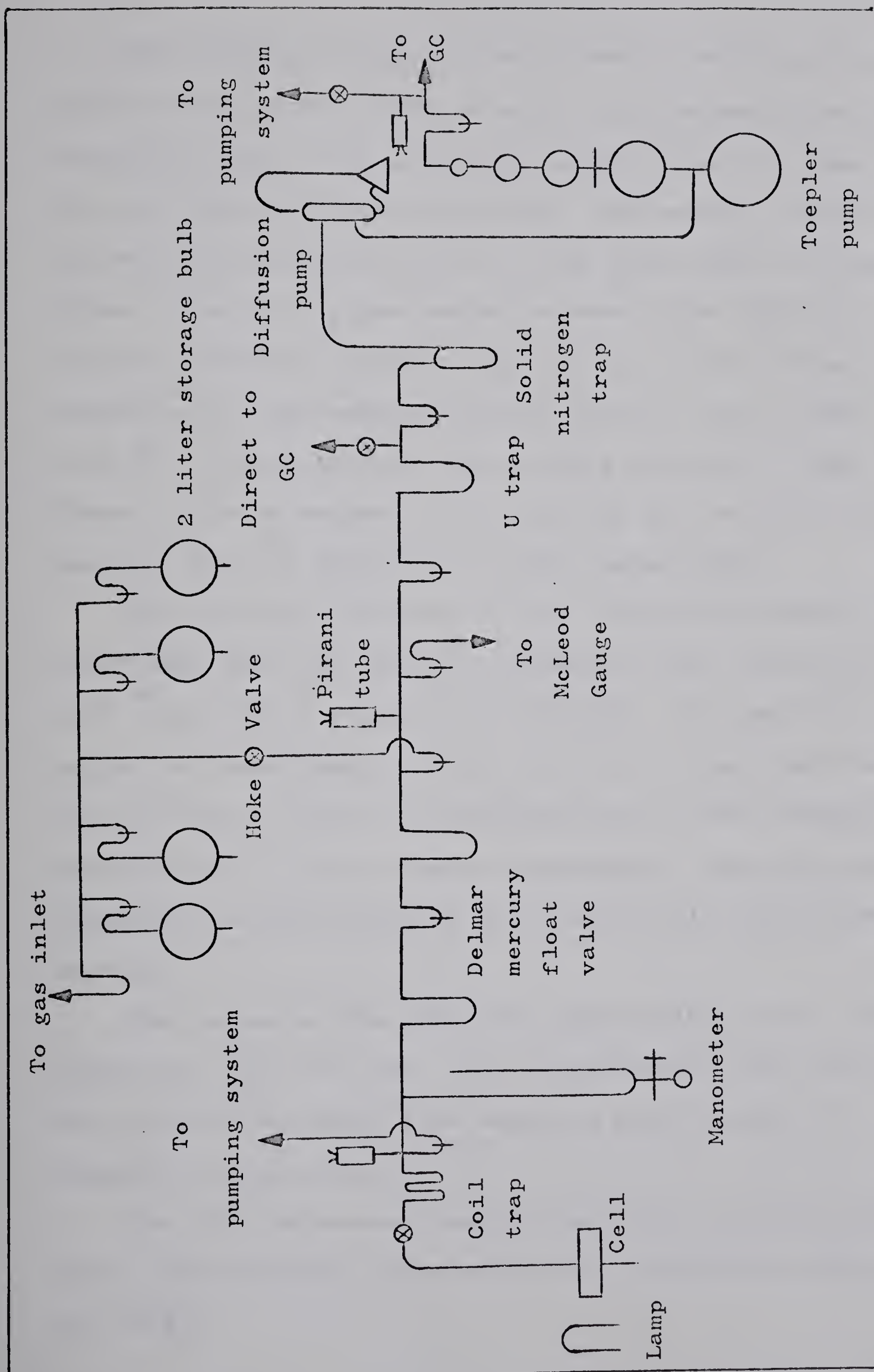


Fig. 1 High Vacuum System





The radiation sources were a Hanovia medium-pressure mercury lamp, model 30620, a spiral high intensity mercury resonance lamp, an 18 watt Osram cadmium spectral lamp and a 25 watt Phillips 93106E zinc lamp. The mercury lamps were operated in conjunction with a 6 mm. thick layer of Vycor #7910 glass. The vycor glass served to remove the  $1849\text{ \AA}$  line from the mercury resonance lamp and limited the effective radiation for the medium-pressure mercury lamp to  $2290\text{--}2550\text{ \AA}$ , the most intense region being centered at  $2490\text{ \AA}$  (65). These limits correspond to the cut-off by the vycor filter and the onset of absorption by COS respectively.

The effective emission of the unfiltered cadmium and zinc lamps were the spectral resonance lines centered at  $2288\text{ \AA}$  and  $2139\text{ \AA}$  respectively (46,65). The lower intensity output of these lamps, a factor of 2 or 3 less than that of the mercury lamps is compensated for by the stronger absorptivity of COS at these wavelengths. Thus the absorbed intensity was approximately the same for all three light sources.

The output of the lamps was reproducible to ca. 3%, except for the zinc lamp. Here measurements were based on the yield of CO rather than exposure time because of intensity fluctuations.

For the temperature studies the quartz cell was placed in an aluminum block furnace with the temperature controlled to  $\pm 0.5^{\circ}\text{C}$ .



### 3) Materials and Purification

- i. Carbonyl sulfide (Matheson) was purified to remove  $\text{CO}_2$  and  $\text{H}_2\text{S}$  impurities by passage through four washing bottles containing concentrated sodium hydroxide solution. The gas was then distilled in vacuo at  $-130^\circ$  (n-pentane slush) and degassed at  $-161^\circ$  (isopentane slush). GC analysis of a purified sample (on a 26-ft., 18% silicone 550 with 2% stearic acid on Celite column, at  $-23^\circ$ , with  $\text{H}_2$  carrier flow of 20 cc/min) failed to indicate the presence of any foreign material.
- ii. Ethylene, propylene, 1-butene and isobutylene (Phillips research grade) were degassed and distilled through two traps at the following temperatures: ethylene at  $-161^\circ$  (isopentane slush), propylene at  $-130^\circ$  (n-pentane slush), 1-butene and isobutylene at  $-117^\circ$  (2-chloropropane slush).
- iii. Vinyl fluoride and 1,1-difluoroethylene (Matheson) were used after degassing and trap-to-trap distillation at  $-161^\circ$  (isopentane slush).
- iv. Cis and trans-1,2-difluoroethylene (Penninsular) isomer separation and purification was effected by GC on a 26-ft., 20% dibutyl maleate on firebrick column operated at  $25^\circ$  and a He flow rate of 100 cc/min. The elution times were 3.9 and 8.2 min. for the trans and cis isomers respectively.



- v. Trifluoroethylene (Penninsular) was purified by GC on a 4-ft. high activity silica gel column at 47° with a He flow rate of 60 cc/min. The elution time was 5.6 min.
- vi. Perfluoroethylene was prepared from the pyrolysis of teflon and purified by trap-to-trap distillation at -130° (n-pentane slush).
- vii. Carbon dioxide, xenon, and carbon monoxide (Airco assayed reagents) were used directly from the one liter bulbs.

#### 4) Gas Chromatography

Gas chromatography was used for quantitative analysis of the sulfur containing products and purification of some of the materials. The basic components, a temperature controlled catharometer (Gow-Mac Model TR III B), a power supply (Gow-Mac Model 9999-C) and a recorder (Sargent Cat. No. S-72180) were arranged for single stream operation. The catharometer was heated to 200°F and a constant filament current of 250 milliamperes was used. The locations of the sampler, column, and product trapping and transferring system are shown in Fig. 2.

Helium (Matheson), dried by passage through a column of Ascarite and indicating drierite, was used as carrier gas. Flow control was attained by an Edwards needle valve and the flow rate measured on an Octoil-S manometer calibrated by a bubble flowmeter.





Drying column of Ascarite  
and indicating Drierite

From

helium

Edwards needle valve

To pumping system

To flow-  
meter

4-way stopcocks

To

Traps

breakseals  
IR gas cell  
NMR tubes

Detector

Column and  
heater

From  
distillation  
train

Fig. 2 Gas Chromatography System





The sampler unit consisted of a U-trap, one 2-lead and two 3-lead cam-operated Hoke valves. After the products were frozen in the trap at  $-196^{\circ}$  (liquid nitrogen) the system was closed by raising the mercury level of the inlet mercury float valve to the bottom of the sampler line. This prevented the loss of material by eliminating any dead space. The products were allowed to thaw and by opening the Hoke valves were swept into the column.

The GC columns were horizontal glass coils of 6 mm. outer diameter. Connection to the apparatus was made by Burrell silicone rubber seals and Type A connectors. Temperature regulation of the column was achieved by an aluminum can wrapped with heating tape. The column packings, lengths, operating conditions and elution times for products are given in Table III. Adequate separation of peaks for accurate analysis was obtained in all cases.

Calibrations for detector response were made for each compound by collecting the products of a reaction individually and measuring several samples in the gas burette. A linear response was found for sample sizes of 0.5 to 5  $\mu$ moles, which was within the range of experimental product yields. Chromatographic peak areas were measured with an Ott planimeter. Calibrations by this method were reproducible to ca. 5% and it was found that variations in detector response for the isomers of a given compound were within this limit.



TABLE III

## GC OPERATING CONDITIONS AND ELUTION TIMES FOR THE SULFUR PRODUCTS

Compound	Column <sup>a</sup>	Flow Rate (cc/min)	Column Temperature (°C)	Elution Time (mins)
vinyl mercaptan	I	50	25	5.0
ethylene episulfide	I	50	25	11.7
	II	50	40	17.6
allyl mercaptan	I	50	37	9.8
	III	60	50	14.0
<u>cis</u> -propene-1-thiol	I	50	37	12.1
	III	60	50	17.2
<u>trans</u> -propene-1-thiol	I	50	37	12.1
	III	60	50	18.7
propylene episulfide	I	50	37	15.6
	III	60	50	21.3
isobutylene episulfide	III	60	57	27.9
2-methylpropene-3-thiol	III	60	57	30.6
2-methylpropene-1-thiol	III	60	57	42.4
1-butene-3-thiol	III	60	60	17.6
1-butene-4-thiol	III	60	60	29.7



TABLE III - continued

Compound	Column	Flow Rate (cc/min)	Column Temperature (°C)	Elution Time (mins)
<u>cis</u> -1-butene-1-thiol	III	60	60	31.5
<u>trans</u> -1-butene-1-thiol	III	60	60	37.0
1-butene episulfide	III	60	60	40.5
<u>trans</u> -2-fluoroethene-1-thiol	II	50	50	9.1
<u>cis</u> -2-fluoroethene-1-thiol	II	50	50	12.4
fluoroethylene episulfide	II	50	50	17.8
	II	50	40	21.4
2,2-difluorovinyl mercaptan	II	50	35	7.4
1,1-difluoroethylene episulfide	II	50	35	10.2
	I	50	25	5.5
<u>trans</u> -1,2-difluoroethylene episulfide	I	50	50	3.4
<u>cis</u> -1,2-difluoroethylene episulfide	I	50	50	8.6
trifluoroethylene episulfide	I	40	25	4.8
	II	50	25	10.9
carbon disulfide	I	40	25	9.1
	II	50	25	13.4

a. Column I = 18% silicone 550, 2% stearic acid on Kromat C; 8 ft. length, 4mm ID

Column II = 25% o-tricresylphosphate on firebrick; 8 ft. length, 4 mm ID

Column III = 10% o-tricresylphosphate on chromosorb W; 16 ft. length, 4 mm ID





Samples of the products were collected from the effluent of the GC for qualitative identification. For mass spectral analysis, samples were transferred in vacuo to break seals and 70 eV spectra were obtained on a Metropolitan Vickers Model MS2 spectrometer. Infrared spectra were obtained on a Perkin Elmer Infracord by transference to a 7.5 cm. micro gas cell. For N.M.R. spectra, obtained on a Varian 100 Mc spectrometer, samples were dissolved in spectral grade carbon tetrachloride with tetramethyl silane as the internal standard.

#### 5) Operational Procedures

After measuring reactant pressures on the mercury manometer, the substrates were distilled into the cell through the vertical coil trap at the lowest possible temperature. This kept the cell free of mercury and prevented any photosensitization reactions. The reactants were allowed to equilibrate for one hour before irradiation. To achieve constant intensity the medium-pressure mercury lamp was operated for one hour before the irradiation; the cadmium, zinc and mercury resonance lamps for 15 min.

In determining  $R^O(CO)$ , the rate of carbon monoxide formation from pure COS, short irradiation times were used to prevent the possibility of reduced absorbed light intensities resulting from the deposition of elemental sulfur on the cell face.



After irradiation, carbon monoxide, the only permanent gas of the reaction, was measured in the gas burette after transference by the Toepler pump in conjunction with the single-stage mercury diffusion pump. Three traps at  $-196^{\circ}$  (liquid nitrogen) retained the excess reactants and sulfur containing products. For the ethylene systems an additional trap at  $-210^{\circ}$  (solid nitrogen) was used. To ensure quantitative recovery of the CO, the condensable materials were alternately warmed and re-frozen twice, the CO being removed each time.

The excess reactants were separated from the sulfur products by distillation through three traps at appropriate low temperatures. The remaining material was transferred directly to the GC sampler for analysis.

Frequent cleaning of the cell was accomplished by admitting air and heating with an oxygen flame. This was necessitated by the deposition of sulfur or polymer on the cell face during irradiation which would reduce the effective light intensity in the next run.



## CHAPTER III

### THE PRODUCTS OF THE REACTION OF SULFUR ATOMS WITH OLEFINS

The gas-phase photodissociation of carbonyl sulfide was utilized for the source of  $S(^1D)$  atoms. The broad absorption spectrum of carbonyl sulfide (1800-2600  $\text{\AA}$ ) lies in a convenient spectral region, readily allowing for irradiation over a wide range of wavelengths. This made practicable the study of the effect of translationally "hot"  $S(^1D)$  atoms on the reaction with olefins (vide infra). In addition, the carbon monoxide from the photodecomposition of COS served as an internal monitor for sulfur atom formation.

The mass spectra of the products are given in Appendix A. The N.M.R. spectra to which references are made, with the exception of those exhibiting single resonance lines, are shown in Appendix B.

#### 1) Ethylene

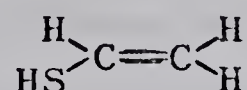
$S(^1D)$  atoms reacted with ethylene to yield two gas chromatographically separable sulfur products (I,II). Their mass spectra showed them to be isomeric addition products,  $C_2H_4S$ , of molecular weight 60.

The N.M.R. spectrum of I showed a doublet in the -SH resonance region at  $\tau$ -values at 7.25 and 7.34. A quartet at  $\tau$ -values of 4.77, 4.82, 4.88, 4.92 (terminal  $=CH_2$





absorption) and a multiplet centered at  $\tau = 3.82$  (non-terminal  $=C<_H$  absorption) appeared in the region for vinylic protons. The integrated peak areas were in the proportion 1:2:1. Thus I was vinyl mercaptan:



Furthermore, the spectrum agrees with that of vinyl mercaptan prepared by the photo-initiated addition of  $\text{H}_2\text{S}$  to acetylene (72).

Product II was identified as ethylene episulfide. Its N.M.R. spectrum consisted of a single peak at  $\tau = 7.73$ . The GC retention time of II was the same as that for a sample of ethylene episulfide prepared by the method of Searles and Lutz (73). A general observation that episulfides are the only products from the  $\text{S}(^3\text{P})$  atom reaction with olefins (69) provided additional confirmation, since II was the only product formed when  $\text{S}(^3\text{P})$  atoms were employed.

## 2) Propylene

Four gas chromatographically-resolvable sulfur products (I,II,III,IV) resulted from the reaction of  $\text{S}(^1\text{D})$  atoms propylene. The mass spectra indicated that all four are addition isomers of molecular weight 74, corresponding to the empirical formula  $\text{C}_3\text{H}_6\text{S}$ .

A first order analysis of the N.M.R. spectrum of compound I showed four regions of absorption: (1) a



multiplet centered at  $\tau=4.1$  (non-terminal  $=C\text{<}_H$  absorption); (2) an overlapping quartet centered at  $\tau=5.0$  (terminal  $=CH_2$  absorption); (3) a triplet in the  $-CH_2-$  region at  $\tau=7.0$ ; and (4) a triplet at  $\tau=8.8$  ( $-SH$  absorption). The I. R. spectrum showed the presence of  $C=C$ ,  $-CH_2-$ , and  $-SH$ . Hence I was identified as allyl mercaptan. Further evidence came from the identical GC retention times of I and an authentic commercial sample of allyl mercaptan.

Products II and III were identified as cis- and trans-propene-1-thiol. Their N.M.R. spectra were similar, showing doublets in the  $-SH$  absorption region at  $\tau$ -values of 7.48 and 7.56. This is characteristic of vinyl mercaptans having an adjacent  $\alpha$  proton (72). Poorly resolved doublets also appeared in the  $-CH_3$  absorption region at  $\tau$ -values of 8.32 and 8.39, again indicative of the presence of an adjacent  $\alpha$  proton. This precludes the possibility of product II or III being the non-terminal vinyl mercaptan propene-2-thiol. The vinylic proton absorptions appeared as a multiplet at a  $\tau$ -value of 4.3.

Attempts to collect product III in sufficient quantities for spin-spin coupling measurements were unsuccessful. However, the coupling constant ( $J=9.6$  c.p.s.) for the vinylic protons in compound II indicated that it was the cis isomer. Trans couplings of this kind are usually somewhat larger. Hence product III probably was trans-propene-1-thiol.





The I.R. spectrum of IV identified it as propylene episulfide. The observed C-H stretching frequencies at 3075 and 3005  $\text{cm}^{-1}$  are characteristic of the thiacyclopropane ring, those in ethylene episulfide appearing at 3080 and 3000  $\text{cm}^{-1}$  (74). Methyl and methylenic absorption occurred at 2895, 2930 and 2980  $\text{cm}^{-1}$ . The ring vibrations of the episulfide ring appeared at 1070  $\text{cm}^{-1}$  in comparison to 1046  $\text{cm}^{-1}$  for ethylene episulfide (74). No C=C absorption was observed. The GC retention time of compound IV was the same as for an authentic sample of propylene episulfide. Again it was the only product formed in the reaction of  $\text{S}(^3\text{P})$  atoms with propylene.

### 3) 1-Butene and Isobutylene

Earlier reports (69) stated that mainly two types of sulfur products, alkenyl mercaptans and episulfides, are formed in the primary reactions of  $\text{S}(^1\text{D})$  atoms with 1-butene and isobutylene. With 1-butene the products were 1-butene-3-thiol (12%), 1-butene-4-thiol (18%) and 1-butene episulfide (70%). Isobutylene gave 2-methylpropene-3-thiol (10%) and isobutylene episulfide (90%) as the only products in low conversion experiments. However, traces of another product, presumed to be 2-methylpropene-1-thiol, appeared at longer exposures.

The apparent absence of vinylic mercaptans in these systems was contrasted to the methylene and isobutylene





reaction. Here the vinyl type insertion isomer, 2-methylbutene-2, accounts for 10-12% of the products formed in the pressure independent region (15,75).

The reactions of  $S(^1D)$  atoms with 1-butene and isobutylene were repeated in order to obtain more accurate data for the relative amounts of vinylic mercaptans formed in these systems. Conversions were comparable to that reported. A longer GC column, 16-ft. vs. 10-ft., was used to analyze the sulfur-containing products. It was of the same material and operated under similar conditions as the previous investigation.

With 1-butene two additional products were found to elute between the 1-butene-4-thiol and 1-butene episulfide peaks. Their mass spectra indicated that they were isomeric with the others and probably are cis- and trans-1-butene-1-thiol by analogy with the propylene system. The improved resolution of the longer GC column probably accounts for the observation of these products. They accounted for 12% of the total sulfur products.

Isobutylene, in addition to the two products reported, gave a third which eluted some twelve minutes after 2-methylpropene-3-thiol. Its mass spectrum indicated that it was isomeric with the other two. As the vinyl mercaptan type product is the only other isomeric structure possible, it has been identified as 2-methylpropene-1-thiol. The



product distribution was isobutylene episulfide 58%, 2-methylpropene-3-thiol 30%, and 2-methylpropene-1-thiol 12%.

#### 4) Vinyl Fluoride

GC partitioning of the condensable fraction showed that three sulfur-containing products (I,II,III) were formed in the reaction of  $S(^{1}D)$  atoms with vinyl fluoride. Their mass spectra showed them to have molecular weights of 78, indicating that they were addition isomers corresponding to the empirical formula  $C_2H_3FS$ .

The N.M.R. spectra of products I and II showed absorptions at  $\tau$ -values of 7.8 and 7.1 respectively. Since the thiol protons of vinyl mercaptans exhibit resonance in this region, I and II will have the vinyl mercaptan type structure. The spectrum of product I also showed vinyl proton absorptions centered at  $\tau$ -values of 3.3 and 4.2. For product II these appeared at  $\tau=3.4$  and 4.75. The coupling constants for these protons in I and II were 13.4 and 4.5 c.p.s. respectively. This indicates that the olefinic protons are vicinally positioned in both I and II; geminal couplings for olefinic protons are somewhat smaller. Hence they probably were terminal vinylic mercaptans. Since trans proton couplings across a double bond are larger than cis couplings, I probably was trans-2-fluoroethene-1-thiol and II cis-2-fluoroethene-1-thiol.





The I.R. spectra of I and II showed the C=C stretching frequency at  $1640\text{ cm}^{-1}$ . This absorption occurs at  $1650\text{--}1645\text{ cm}^{-1}$  for vinyl fluoride (76). The C-F stretching mode appeared at  $1130\text{ cm}^{-1}$  for both products.

Compound III was identified as fluoroethylene episulfide. The N.M.R. spectrum of III showed three regions of absorption at  $\tau$ -values of 4.1, 7.4 and 7.6. These correspond to the absorptions by the three hydrogen atoms in fluoroethylene episulfide. The absorption by the proton on the terminal carbon atom ( $\begin{smallmatrix} \text{F} \\ \diagup \\ \text{H}-\text{C}=\end{smallmatrix}$ ) is shifted to lower field because of the presence of the highly electronegative F atom at the same centre.

No C=C absorption appeared in the I.R. spectrum of III. The C-F stretching frequency occurred at  $1170\text{ cm}^{-1}$  and the episulfide ring deformation at  $1020\text{ cm}^{-1}$ .

#### 5) 1,1-Difluoroethylene

GC analysis of the condensable fraction showed that two sulfur-containing products (I,II) were formed in the reaction of  $\text{S}(^1\text{D})$  atoms with 1,1-difluoroethylene. Their mass spectra showed them to be isomers with molecular weights of 96 ( $\text{C}_2\text{F}_2\text{H}_2\text{S}$ ).

The N.M.R. spectrum of I showed a multiplet, centered at a  $\tau$ -value of 7.76, in the thiol-proton region for vinyl mercaptans. Hence I has been identified as 2,2-difluorovinyl





mercaptan. The vinyl hydrogen atom absorption also appeared as a multiplet at  $\tau=5.3$ , being split to four sets of doublets through coupling to -SH and cis and trans F atoms.

The I.R. spectrum of I showed C=C absorption at  $1710\text{ cm}^{-1}$ . For 1,1-difluoroethylene this absorption occurs at  $1730\text{ cm}^{-1}$  (76). The C-F stretching frequencies of the =CF<sub>2</sub> group appeared at 1325 and  $1190\text{ cm}^{-1}$ .

Product II was identified as 1,1-difluoroethylene episulfide. Its N.M.R. spectrum consisted of a single peak at a  $\tau$ -value of 7.2. Apparently an uncommon coincidence of coupling constants caused the peaks to coalesce to a single, narrow line with the outer satellite peaks being too small to be observed. Further confirmation of identification came from the fact that it was the only product formed when S(<sup>3</sup>P) atoms were employed.

#### 6) Cis- and Trans-1,2-Difluoroethylene

Both cis- and trans-1,2-difluoroethylene reacted with S(<sup>1</sup>D) atoms to yield two sulfur-containing products. Their mass spectra showed that they were addition isomers of molecular weight 96, corresponding to the empirical formula C<sub>2</sub>F<sub>2</sub>H<sub>2</sub>S.

The GC retention times for the two compounds resulting from the cis olefin-S(<sup>1</sup>D) atom system were identical to those formed in the trans olefin-S(<sup>1</sup>D) atom system. This



indicated that the products were the same in the two systems. This was verified by preparing samples of the products for N.M.R. analysis from an equal mixture of the cis and trans olefins. The N.M.R. spectra of the GC separated products showed that only two sulfur addition compounds were formed. The spectra, centered at a  $\tau$ -value of 4.2, showed the complex, symmetrical structure characteristic of AA'XX' systems. Also no absorption appeared in the region for thiol proton resonance. Hence the products probably were trans and cis-1,2-difluoroethylene episulfide.

The first product to elute from the GC column was predominant (80% of the total) in the reaction of S( $^1\text{D}$ ) atoms with trans-1,2-difluoroethylene. In the cis-1,2-difluoroethylene - S( $^1\text{D}$ ) atom system the second compound to elute represented 98% of the total products. Thus, by analogy with the S( $^1\text{D}$ ) atom - 2-butene systems, where the addition reaction is highly stereospecific (69), the trans structure was assigned to the first product to elute from the GC column.

#### 7) Trifluoroethylene

GC analysis showed that only one addition product resulted from the reaction of S( $^1\text{D}$ ) or S( $^3\text{P}$ ) atoms with trifluoroethylene. Its mass spectrum showed that it had a molecular weight of 114, corresponding to the empirical formula  $\text{C}_2\text{F}_3\text{HS}$ .





Since the N.M.R. spectrum of the product showed no thiol-proton absorption, it was identified as trifluoroethylene episulfide. The absorption by the single proton occurred at a  $\tau$ -value centered at 4.1. Couplings to trans and geminal fluorine atoms split the absorption peak to a quartet.

Small amounts of a decomposition product were also observed by GC analysis. It has been identified as carbon disulfide by comparison of its mass spectrum and GC retention time with that of an authentic commercial sample.

#### 8) Tetrafluoroethylene

No volatile products were recovered from the reaction of  $S(^1D)$  or  $S(^3P)$  atoms with tetrafluoroethylene. The only product was a white solid deposited on the walls of the reaction vessel. In-vacuo pyrolysis of the solid yielded small amounts of a condensable gas which was shown to be tetrafluoroethylene by its mass spectrum. However, a  $C_2F_4S$  adduct has been observed from the  $C_2F_4-S(^1D)$  reaction by the method of flash photolysis-kinetic mass spectrometry (85). The oscillogram indicated a half-life of ca. 10 seconds for the adduct which probably was tetrafluoroethylene episulfide. Apparently this product is unstable and is rapidly consumed by a polymerization process, as evidenced by the pyrolysis of the solid formed during the reaction in the static system.





Table IV summarizes the product distributions for a number of olefin-S(<sup>1</sup>D) atom systems. The episulfide type addition product was formed in all systems, except for tetrafluoroethylene where no products were observed. Vinylic type mercaptan products were only observed with those olefins having a terminal =CH<sub>2</sub> group. Alkenyl type mercaptans formed with all olefins containing methyl group substituents.



TABLE IV

PRODUCT DISTRIBUTIONS FOR OLEFIN-S(<sup>1</sup>D) ATOM SYSTEMS<sup>a</sup>

Olefin	% Distribution		
	Vinyl Type	Alkenyl Type	Episulfide
	Mercaptan(s)	Mercaptan(s)	
Ethylene	49	..	51
Propylene	19	19	62
Isobutylene	12	32	56
2-Butenes <sup>b</sup>	0	32	68
1-Butene	12	29	59
Trimethylethylene <sup>c</sup>	0	42	58
Tetramethylethylene <sup>c</sup>	..	50	50
Vinyl Fluoride	32	..	68
1,1-Difluoroethylene	31	..	69
1,2-Difluoroethylenes	0	..	100
Trifluoroethylene	0	..	100
Tetrafluoroethylene	..	..	0

<sup>a</sup>All data refers to the pressure-independent region, i.e.

P<400 torr and Hg-arc photolysis.

<sup>b</sup>From reference 69.

<sup>c</sup>From reference 70.



## CHAPTER IV

### THE EFFECT OF OLEFIN PRESSURE ON THE REACTIONS OF SULFUR ATOMS WITH OLEFINS

#### 1) Kinetic features

The effect of olefin pressure on the rates of product formation in the COS-olefin system is shown for the ten olefins studied in Tables V - XV and Figs. 3 - 5. The following kinetic features are characteristic for all these systems: (a) with increasing olefin pressure the rate of CO formation gradually decreases to a value nearly half of that from pure COS; (b) there is a simultaneous increase in the rate of product formation to a limiting flat maximum; and (c) in those systems where mercaptans are formed, the ratio  $R(\text{mercaptan})/R(\text{episulfide})$  attains a limiting value at higher olefin pressures.

#### 2) Mechanism of the reaction

To explain the increase in rate of product formation and simultaneous decrease in  $R(\text{CO})$  the following primary reactions are considered:

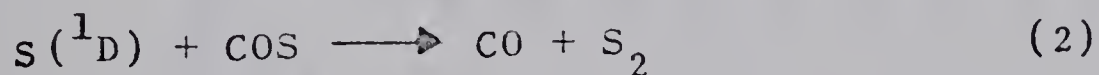
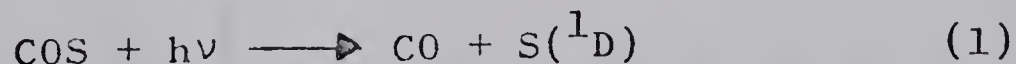






TABLE V

VARIATION IN PRODUCT RATES WITH  $C_2H_4$  PRESSURE IN THE  $COS-C_2H_4$  SYSTEM<sup>a</sup>

$P(C_2H_4)$ , torr	Rates, $\mu\text{moles/min.} \times 10$						$\frac{R(VM)}{R(ES)}$	%recovery <sup>c</sup>
	CO	$VM^b$	$ES^b$	$\Sigma R$ (VM, ES)	$CO^O-CO$			
0	3.01	-	-	-	-	-	-	-
25	2.27	0.21	0.30	0.51	0.74	0.70	69	
50	2.08	0.28	0.41	0.69	0.93	0.68	75	
100	1.99	0.42	0.53	0.95	1.02	0.78	93	
200	1.80	0.48	0.56	1.04	1.21	0.86	86	
300	1.73	0.50	0.57	1.07	1.28	0.89	84	
400	1.67	0.54	0.57	1.11	1.34	0.94	82	
600	1.64	0.56	0.59	1.15	1.37	0.95	84	
800	1.57	0.57	0.60	1.17	1.44	0.95	82	

<sup>a</sup> $P(COS) = 100$  torr; exposure time = 30 min.; light source, med. pressure Hg arc<sup>b</sup> $VM$  = vinyl mercaptan;  $ES$  = ethylene episulfide<sup>c</sup>%recovery of condensables in terms of  $R^O(CO)-R(CO)$



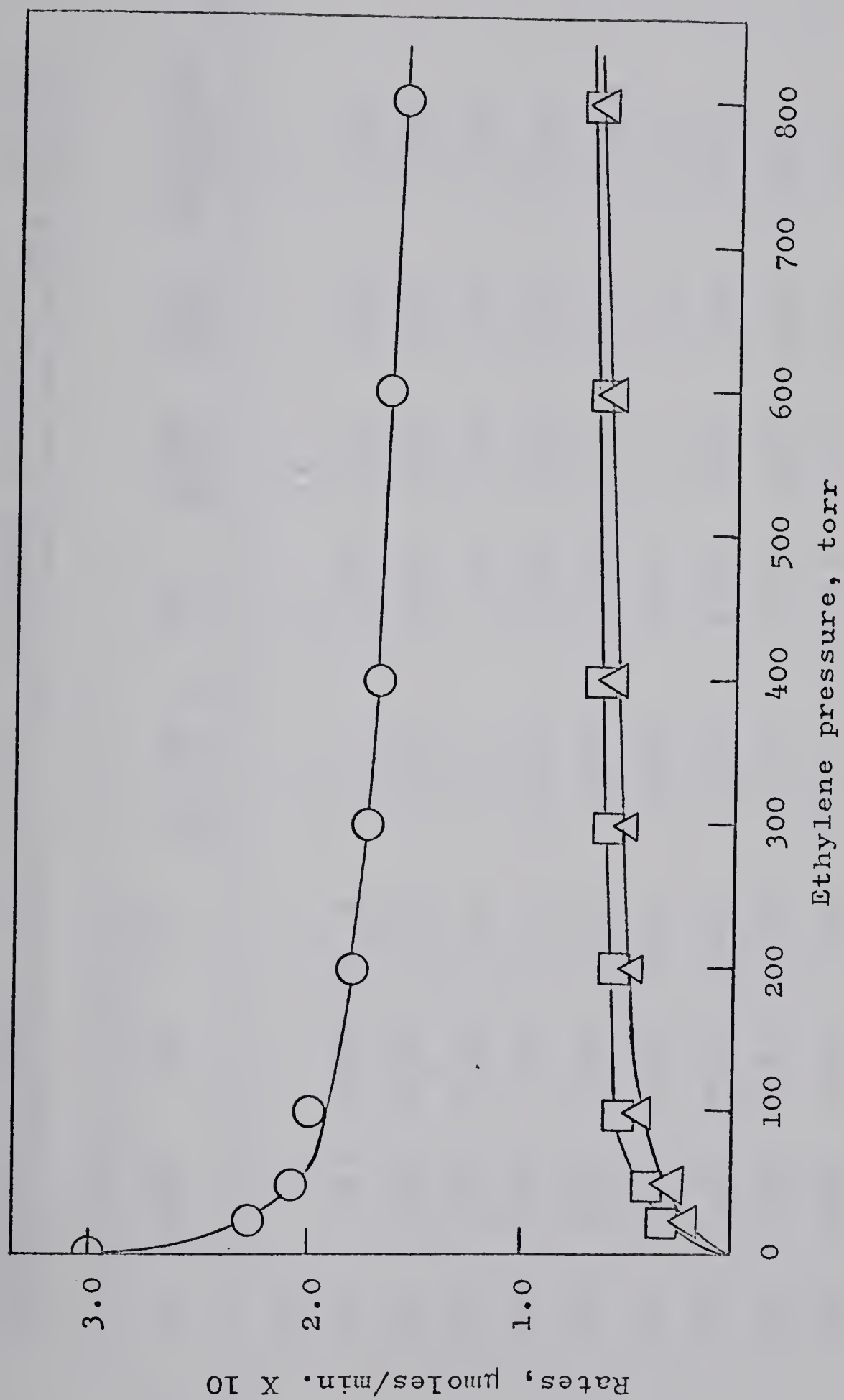


Fig. 3 Rates of product formation as a function of ethylene pressure in the COS-ethylene system.  $\bigcirc$  = CO;  $\triangle$  = vinyl mercaptan;  $\square$  = ethylene episulfide



TABLE VI

VARIATION IN PRODUCT RATES WITH  $C_3H_6$  PRESSURE IN THE  $COS-C_3H_6$  SYSTEM<sup>a</sup>

P(C <sub>3</sub> H <sub>6</sub> ), torr	Rates, μmoles/min. X 10										% recovery <sup>c</sup>
	CO	MVM <sup>b</sup>	AM <sup>b</sup>	PS <sup>b</sup>	ΣR (MVM, AM, PS)	CO <sup>o</sup> -CO	$\frac{R(MVM)}{R(PS)}$	$\frac{R(AM)}{R(PS)}$	$\frac{\Sigma R(MVM, AM)}{R(PS)}$		
0	2.12	-	-	-	-	-	-	-	-	-	
25	1.57	0.05	0.05	0.34	0.44	0.55	0.14	0.14	0.28	81	
51	1.48	0.06	0.05	0.37	0.48	0.64	0.16	0.13	0.29	74	
103	1.36	0.08	0.08	0.38	0.54	0.75	0.22	0.20	0.42	71	
205	1.28	0.09	0.10	0.41	0.60	0.84	0.22	0.24	0.46	72	
305	1.25	0.08	0.10	0.45	0.63	0.87	0.19	0.23	0.42	73	
406	1.20	0.08	0.09	0.45	0.62	0.92	0.17	0.21	0.38	67	
505	1.11	0.11	0.12	0.47	0.70	1.00	0.24	0.26	0.50	70	
604	1.11	0.10	0.13	0.48	0.71	1.00	0.20	0.27	0.47	70	
802	1.09	0.11	0.12	0.49	0.72	1.03	0.22	0.25	0.47	70	

<sup>a</sup>P(COS) = 100 torr; exposure time = 30 min.; light source, med. pressure Hg arc<sup>b</sup>MVM = cis + trans-propene-1-thiol; AM = allyl mercaptan; PS = propylene episulfide<sup>c</sup>%recovery of condensables in terms of  $R^o(CO)-R(CO)$





TABLE VII

VARIATION IN PRODUCT RATES WITH  $C_3H_6$  PRESSURE IN THE  $COS-C_3H_6$  SYSTEM<sup>a</sup>

$P(C_3H_6)$ , torr	CO $\mu\text{moles/min.} \times 10$	$\sqrt{\frac{R(AM)^b}{R(CO)} \times 10 \frac{R(cPT)^b}{R(CO)}}$						$\frac{R(\Sigma M)^b}{R(PS)}$	$\frac{R(cPT)}{R(tPT)}$	$\frac{R(\Sigma C_3H_6S)}{R(CO)}$
		$\frac{R(AM)^b}{R(CO)}$	$\frac{R(cPT)^b}{R(CO)}$	$\frac{R(tPT)^b}{R(CO)}$	$\frac{R(PS)^b}{R(CO)}$	$\frac{R(PS)^b}{R(CO)}$	$\frac{R(PS)^b}{R(CO)}$			
26	3.38	0.54	0.35	0.17	2.37	0.45	2.05	0.34		
52	3.05	0.70	0.51	0.29	2.82	0.53	1.78	0.42		
77	2.74	0.89	0.59	0.33	3.02	0.60	1.77	0.50		
101	2.53	0.89	0.59	0.31	3.26	0.55	1.90	0.51		
126	2.41	1.10	0.70	0.39	3.32	0.66	1.80	0.55		
151	2.29	1.24	0.77	0.47	3.52	0.71	1.65	0.60		
176	2.33	1.22	0.71	0.44	3.52	0.67	1.63	0.59		
201	2.20	1.32	0.76	0.50	3.61	0.71	1.54	0.62		
250	2.14	1.38	0.78	0.50	3.83	0.69	1.56	0.65		
300	2.01	1.48	0.78	0.52	4.07	0.68	1.51	0.69		
400	1.95	1.54	0.76	0.53	3.87	0.73	1.43	0.67		

<sup>a</sup> $p(COS) = 100$  torr; exposure time = 20 min.; light source, Zn spectral lamp<sup>b</sup> $AM$  = allyl mercaptan;  $tPT$  = trans-propene-1-thiol;  $cPT$  = cis-propene-1-thiol; $PS$  = propylene episulfide;  $R(\Sigma M) = \Sigma R(AM, tPT, cPT)$



TABLE VIII

VARIATION IN PRODUCT RATES WITH  $i\text{-C}_4\text{H}_8$  PRESSURE IN THE  $\text{COS-i-C}_4\text{H}_8$  SYSTEM<sup>a</sup>

P(i-C <sub>4</sub> H <sub>8</sub> ), torr	Rates, μmoles/min. X 10						CO <sup>o</sup> -CO	ΣR (BM, BV, BS)	$\frac{R(BM)}{R(BS)}$	$\frac{R(BV)}{R(BS)}$	$\frac{\Sigma R(BM, BV)}{R(BS)}$	% recovery <sup>c</sup>
	CO	BM <sup>b</sup>	BV <sup>b</sup>	BS <sup>b</sup>								
0	5.13	-	-	-	-	-	-	-	-	-	-	-
50	3.19	0.39	0.18	1.25	1.82	1.94	0.31	0.14	0.44	94		
100	2.99	0.45	0.20	1.24	1.89	2.14	0.36	0.16	0.52	88		
200	2.82	0.58	0.25	1.32	2.15	2.31	0.44	0.19	0.63	93		
500	2.74	0.62	0.25	1.24	2.11	2.39	0.50	0.20	0.70	88		
600	2.73	0.73	0.28	1.30	2.31	2.40	0.56	0.22	0.78	96		

<sup>a</sup> $P(\text{COS}) = 100$  torr; exposure time = 15 min.; light source, med. pressure Hg arc

<sup>b</sup>BM = 2-methylpropene-3-thiol; BV = 2-methylpropene-1-thiol; BS = isobutylene episulfide

<sup>c</sup>% recovery of condensables in terms of  $R^o(\text{CO})-R(\text{CO})$



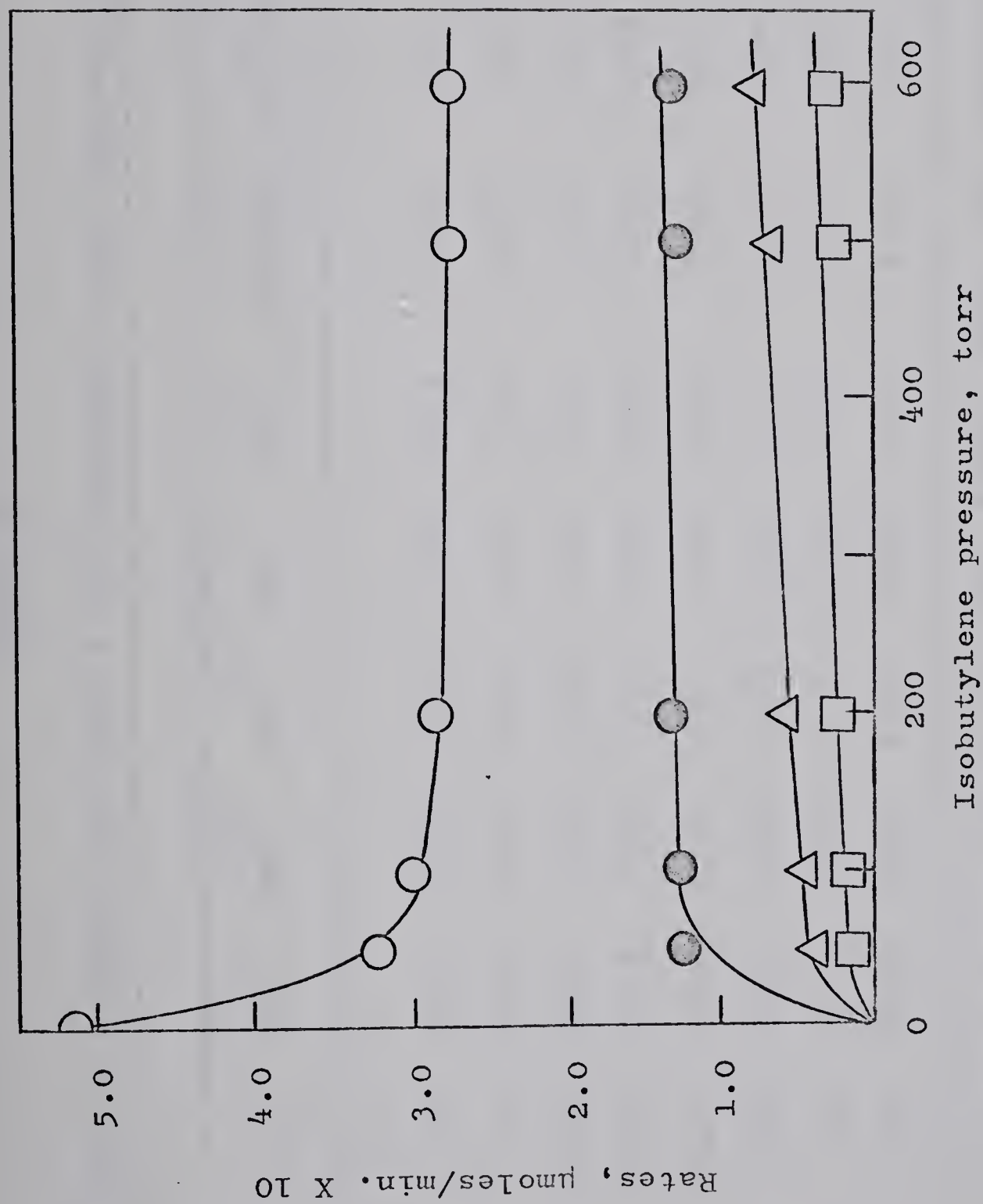


Fig. 4 Rates of product formation as a function of isobutylene pressure in the COS-isobutylene system.  $\Delta$  = 2-methylpropene-3-thiol;  $\square$  = 2-methylpropene-1-thiol;

● = isobutylene episulfide; ○ = CO





TABLE IX

VARIATION IN PRODUCT RATES WITH 1-C<sub>4</sub>H<sub>8</sub> PRESSURE IN THE COS-1-C<sub>4</sub>H<sub>8</sub> SYSTEM<sup>a</sup>

P(1-C <sub>4</sub> H <sub>8</sub> ), torr	Rates, $\mu\text{moles/min.} \times 10$							% recovery <sup>c</sup>
	CO	BM1 <sup>b</sup>	BM2 <sup>b</sup>	cBV <sup>b</sup>	tBV <sup>b</sup>	BS <sup>b</sup>	$\Sigma R(C_4H_8S)$	CO <sup>o</sup> -CO
0	4.71	-	-	-	-	-	-	-
50	3.06	0.12	0.16	0.10	0.040	1.13	1.55	1.65
100	2.91	0.16	0.21	0.11	0.047	1.15	1.68	1.80
100	2.86	0.17	0.23	0.12	0.053	1.16	1.73	1.85
200	2.75	0.19	0.29	0.14	0.067	1.14	1.83	1.96
300	2.71	0.21	0.31	0.15	0.067	1.16	1.90	2.00
400	2.62	0.21	0.31	0.15	0.069	1.13	1.87	2.09
500	2.62	0.24	0.34	0.16	0.074	1.21	2.02	2.09
600	2.59	0.25	0.35	0.16	0.083	1.19	2.03	2.12

<sup>a</sup>P(COS) = 100 torr; exposure time = 20 min.; light source, med. pressure Hg arc<sup>b</sup>BM1 = 1-butene-3-thiol; BM2 = 1-butene-4-thiol; tBV = trans-1-butene-1-thiol;cBV = cis-1-butene-1-thiol; BS = 1-butene episulfide<sup>c</sup>% recovery of condensables in terms of R<sup>o</sup>(CO)-R(CO)



TABLE IX cont.

$P(1-C_4H_8),$ $t_{orr}$	$\frac{R(BM1)}{R(BS)}$	$\frac{R(BM2)}{R(BS)}$	$\frac{R(cBV)}{R(BS)}$	$\frac{R(tBV)}{R(BS)}$	$\frac{R(BM2)}{R(BM1)}$	$\frac{R(cBV)}{R(tBV)}$	$\frac{R(\Sigma M)^d}{R(BS)}$
50	0.11	0.14	0.089	0.035	1.3	2.7	0.37
100	0.14	0.18	0.096	0.041	1.3	2.3	0.46
100	0.15	0.20	0.10	0.045	1.4	2.3	0.49
200	0.17	0.25	0.13	0.058	1.5	2.1	0.61
300	0.18	0.27	0.13	0.058	1.5	2.2	0.64
400	0.19	0.28	0.13	0.061	1.5	2.2	0.66
500	0.20	0.28	0.13	0.061	1.4	2.1	0.67
600	0.21	0.29	0.14	0.070	1.4	1.9	0.71

$$^d R(\Sigma M) = \Sigma R(BM1, BM2, tBV, cBV)$$



TABLE X

VARIATION IN PRODUCT RATES WITH  $C_2H_3F$  PRESSURE IN THE  $COS-C_2H_3F$  SYSTEM<sup>a</sup>

P( $C_2H_3F$ ), torr	Rates, $\mu\text{moles/min.} \times 10$							% recovery <sup>c</sup>
	CO	tVM <sup>b</sup>	cVM <sup>b</sup>	VES <sup>b</sup>	$\Sigma R(tVM, cVM, ES)$	CO <sup>o</sup> -CO	$\frac{\Sigma R(tVM, cVM)}{R(VES)}$	
0	4.41	-	-	-	-	-	-	-
50	2.90	0.06	0.08	0.65	0.79	1.51	0.22	54
100	2.63	0.10	0.13	0.75	0.98	1.78	0.31	57
200	2.47	0.15	0.17	0.84	1.16	1.94	0.38	61
300	2.32	0.17	0.20	0.87	1.24	2.09	0.43	60
400	2.29	0.19	0.21	0.91	1.31	2.12	0.44	64
600	2.24	0.21	0.22	0.92	1.35	2.17	0.48	63
800	2.20	0.22	0.23	0.99	1.44	2.21	0.45	66

<sup>a</sup>P(COS) = 100 torr; exposure time = 15 min.; light source, med. pressure Hg arc<sup>b</sup>tVM = trans-2-fluoroethene-1-thiol; cVM = cis-2-fluoroethene-1-thiol;

VES = fluoroethylene episulfide

<sup>c</sup>% recovery of condensables in terms of  $R^o(CO)-R(CO)$





TABLE XI

VARIATION IN PRODUCT RATES WITH  $\text{CF}_2\text{CH}_2$  PRESSURE IN THE  $\text{COS}-\text{CF}_2\text{CH}_2$  SYSTEM<sup>a</sup>

$\text{P}(\text{CF}_2\text{CH}_2)$ , torr	Rates, $\mu\text{moles/min.} \times 10$					$\frac{\text{R}(\text{DFVM})}{\text{R}(\text{DFES})}$	% recovery <sup>c</sup>
	CO	DFVM <sup>b</sup>	DFES <sup>b</sup>	$\Sigma \text{R}(\text{DFVM}, \text{DFES})$	$\text{CO}^{\circ}-\text{CO}$		
0	4.43	-	-	-	-	-	-
50	2.95	0.07	0.53	0.60	1.48	0.13	41
100	2.71	0.20	0.77	0.97	1.71	0.26	54
200	2.53	0.30	0.81	1.11	1.89	0.37	59
300	2.43	0.33	0.86	1.19	2.00	0.38	60
400	2.33	0.38	0.90	1.28	2.09	0.42	61
600	2.25	0.38	0.93	1.31	2.17	0.41	60
800	2.21	0.39	0.87	1.26	2.21	0.45	58

<sup>a</sup> $\text{P}(\text{COS}) = 100$  torr; exposure time = 15 min.; light source, med. pressure Hg arc<sup>b</sup>DFVM = 2,2-difluorovinyl mercaptan; DFES = 1-difluoroethylene episulfide<sup>c</sup>% recovery of condensables in terms of  $\text{R}^{\circ}(\text{CO})-\text{R}(\text{CO})$



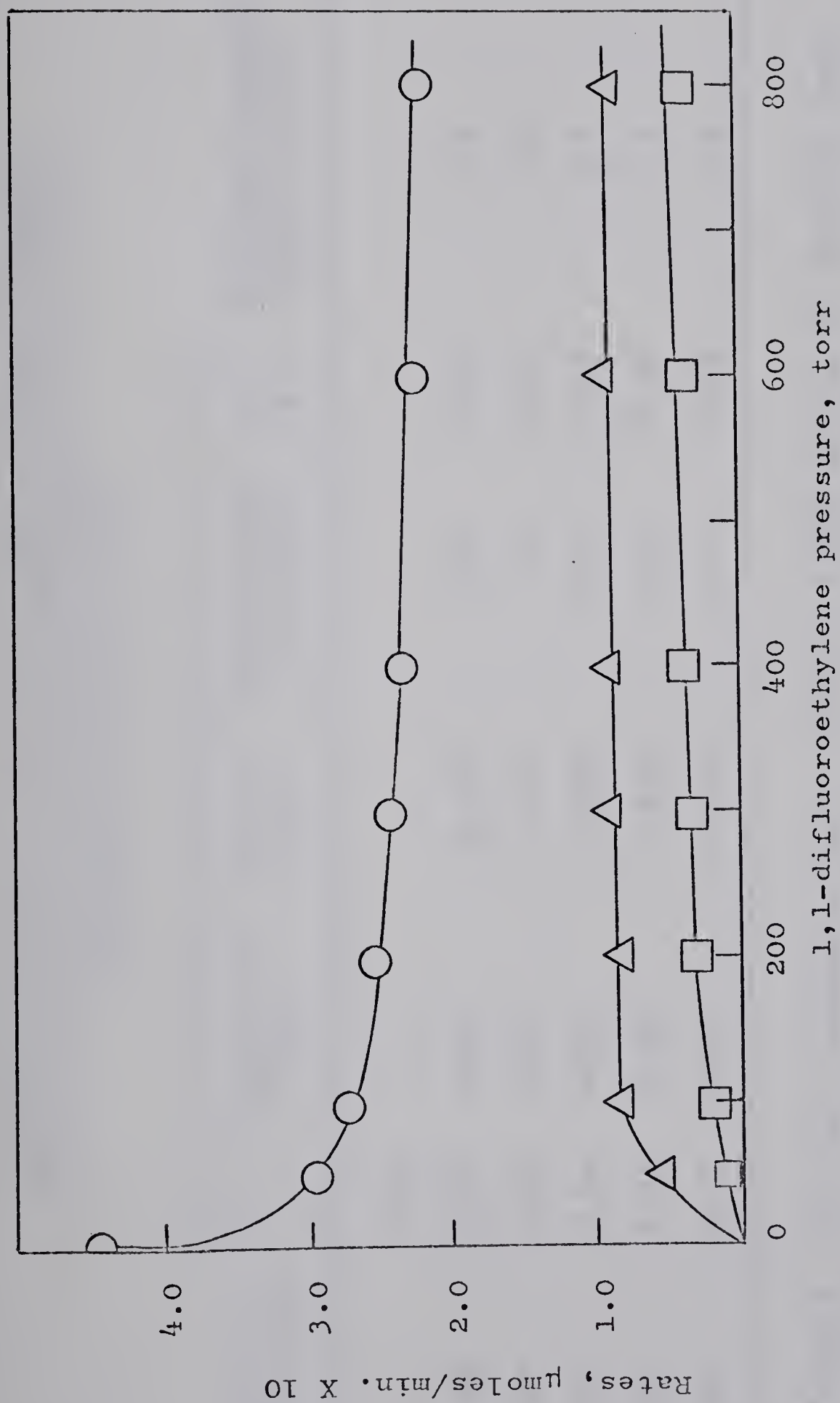


Fig. 5 Rates of product formation as a function of 1,1-difluoroethylene pressure in the COS-1,1-difluoroethylene system.  $\square$  = 2,2-difluorovinyl mercaptan;  $\triangle$  = 1,1-difluoroethylene episulfide;  $\circ$  = CO



TABLE XII

VARIATION IN PRODUCT RATES WITH trans-1,2-CFHCFH PRESSURECOS-trans-1,2-CFHCFH SYSTEM<sup>a</sup>

P( <u>trans</u> -1,2- CFHCFH), torr	CO	<u>trans</u> -1,2- DFES	Rates, $\mu\text{moles/min.} \times 10$				%recovery <sup>c</sup>
			<u>cis</u> -1,2- DFES	$\Sigma R(\text{cis+trans-}$ 1,2-DFES)	CO <sup>o</sup> -CO	$\frac{R(\text{trans-1,2-DFES})}{R(\text{cis-1,2-DFES})}$	
0	1.30	-	-	-	-	-	-
50	0.97	0.15	0.037	0.19	0.33	4.0	58
150	0.85	0.18	0.047	0.23	0.45	3.9	51
200	0.84	0.22	0.050	0.27	0.46	4.3	59
300	0.81	0.23	0.053	0.28	0.49	4.2	57
400	0.77	0.23	0.053	0.28	0.53	4.3	53

<sup>a</sup>P(COS) = 100 torr; exposure time = 30 min.; light source, Cd spectral lamp<sup>b</sup>DFES = difluoroethylene episulfide<sup>c</sup>%recovery of condensables in terms of R<sup>o</sup>(CO)-R(CO)





TABLE XIII

VARIATION IN PRODUCT RATES WITH cis-1,2-CFHCFH PRESSURECOS-cis-1,2-CFHCFH SYSTEM<sup>a</sup>

P( <u>cis</u> -1,2- CFHCFH), torr	Rates, $\mu\text{moles/min.} \times 10$					% recovery <sup>c</sup>
	CO	<u>cis</u> -1,2- DFES <sup>b</sup>	<u>trans</u> -1,2- DFES	$\Sigma R(\frac{\text{trans+cis-}}{1,2\text{-DFES}})$	CO <sup>o</sup> -CO	
0	1.42	-	-	-	-	-
50	1.02	0.087	0.002	0.089	0.40	22
100	0.90	0.13	0.002	0.13	0.52	24
200	0.79	0.15	0.002	0.15	0.63	24
300	0.71	0.17	0.002	0.17	0.71	24
600	0.70	0.18	0.002	0.18	0.72	26
800	0.70	0.22	0.003	0.22	0.72	31

<sup>a</sup>P(COS) = 100 torr; exposure time = 30 min.; light source, Cd spectral lamp<sup>b</sup>DFES = difluoroethylene episulfide<sup>c</sup>% recovery of condensables in terms of R<sup>o</sup>(CO)-R(CO)



TABLE XIV

VARIATION IN PRODUCT RATES WITH  $C_2F_3H$  PRESSURE IN THE  $COS-C_2F_3H$  SYSTEM<sup>a</sup>

$P(C_2F_3H)$ , torr	Rates, $\mu\text{moles/min.} \times 10$					% recovery of TFES <sup>c</sup>
	CO	TFES <sup>b</sup>	$CS_2$	$CO^O-CO$		
0	1.81	-	-	-		-
50	1.35	0.12	0.03	0.46		31
100	1.18	0.16	0.02	0.63		25
200	1.11	0.17	0.02	0.70		24
300	1.07	0.18	0.02	0.74		24
400	1.06	0.23	0.02	0.75		31
600	0.98	0.23	0.02	0.83		28
800	0.93	0.22	0.01	0.88		25

<sup>a</sup> $P(COS) = 100$  torr; exposure time = 30 min.; light source, Cd spectral lamp

<sup>b</sup>TFES = trifluoroethylene episulfide

<sup>c</sup>% recovery of TFES in terms of  $R^O(CO)-R(CO)$



TABLE XV

VARIATION IN CO<sup>a</sup> RATES WITH C<sub>2</sub>F<sub>4</sub> PRESSURE  
IN THE COS-C<sub>2</sub>F<sub>4</sub> SYSTEM<sup>b</sup>

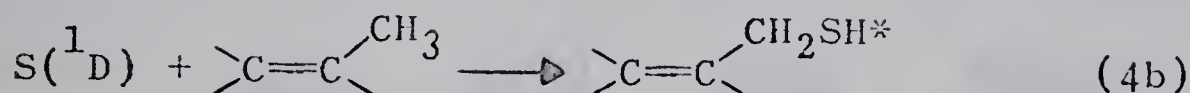
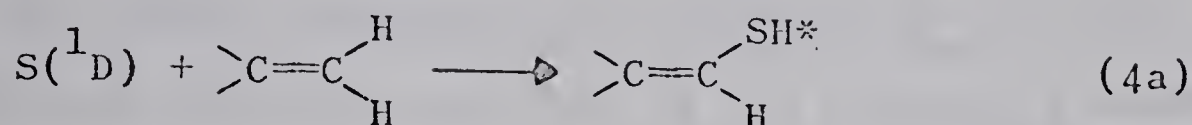
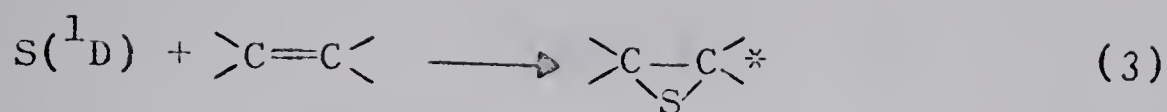
P(C <sub>2</sub> F <sub>4</sub> ), torr	Rates, $\mu\text{moles/min.} \times 10^{-}$	
	CO	CO <sup>O</sup> -CO
0	1.73	-
25	1.62	0.11
50	1.29	0.44
75	1.20	0.53
125	1.23	0.50
150	1.11	0.62
175	1.07	0.66
200	1.00	0.73
300	1.02	0.71
400	1.08	0.65
600	1.01	0.72
800	0.99	0.74

<sup>a</sup>No other volatile products formed except for a trace of CS<sub>2</sub>

<sup>b</sup>P(COS) = 100 torr; exposure time = 30 min.; light source, Cd spectral lamp







The competition for sulfur atoms by the olefin in steps 3, 4a and 4b would account for  $R(CO)$  falling to one-half of its value in the absence of olefin. The rates of sulfur product formation will be equivalent to the decrease in rate of carbon monoxide formation,  $R^O(CO)-R(CO)$ , and reach a limiting value of  $R^O(CO)/2$ , where  $R^O(CO)$  is the rate of carbon monoxide formation in the absence of olefin. Product recoveries, based on  $R^O(CO)-R(CO)$ , were, however, less than 100%. Several factors such as mechanical handling, secondary photolysis and secondary reactions would account for the incomplete product recovery.

The magnitude of the secondary photodecomposition of products can be seen from Table XVI and Figs. 6 - 8 for the  $C_2H_4$  system. At longer exposures the yields, relative to  $R(CO)$ , of both vinyl mercaptan and ethylene episulfide decrease with all three light sources employed. It is apparent that vinyl mercaptan is relatively more sensitive to secondary photolysis than is ethylene episulfide. Secondary photodecomposition is less important for the Cd lamp since COS has a high absorptivity at  $\lambda$  2288 Å. Photodecomposition



TABLE XVI

RATES OF PRODUCT FORMATION AS A FUNCTION OF CO YIELD AND WAVE-  
LENGTH OF EXCITING RADIATION IN THE COS-C<sub>2</sub>H<sub>4</sub> SYSTEM<sup>a</sup>

Light Source	CO, μmoles	$\frac{R(VM)}{R(CO)}$ <sup>b</sup>	$\frac{R(ES)}{R(CO)}$ <sup>b</sup>	$\frac{\Sigma R(VM, ES)}{R(CO)}$	$\frac{R(VM)}{R(ES)}$
med. pressure	5.35	0.320	0.331	0.651	0.97
Hg arc	8.07	0.296	0.312	0.608	0.94
(2537, 2490 Å.)	10.55	0.274	0.312	0.586	0.88
	13.34	0.250	0.311	0.561	0.80
Cd spectral	4.52	0.436	0.284	0.720	1.55
lamp	7.39	0.420	0.276	0.696	1.52
(2288 Å.)	12.11	0.415	0.279	0.694	1.48
	17.85	0.378	0.272	0.650	1.39
Zn spectral	4.03	0.402	0.283	0.685	1.42
lamp	8.58	0.326	0.265	0.591	1.23
(2139 Å.)	10.33	0.304	0.254	0.558	1.19
	14.80	0.260	0.253	0.513	1.03

<sup>a</sup>P(COS) = 100 torr; P(C<sub>2</sub>H<sub>4</sub>) = 400 torr; measurements based on CO yield so as not to include reduced light intensities resulting from depositions of polymers or S on the cell face

<sup>b</sup>VM = vinyl mercaptan; ES = ethylene episulfide



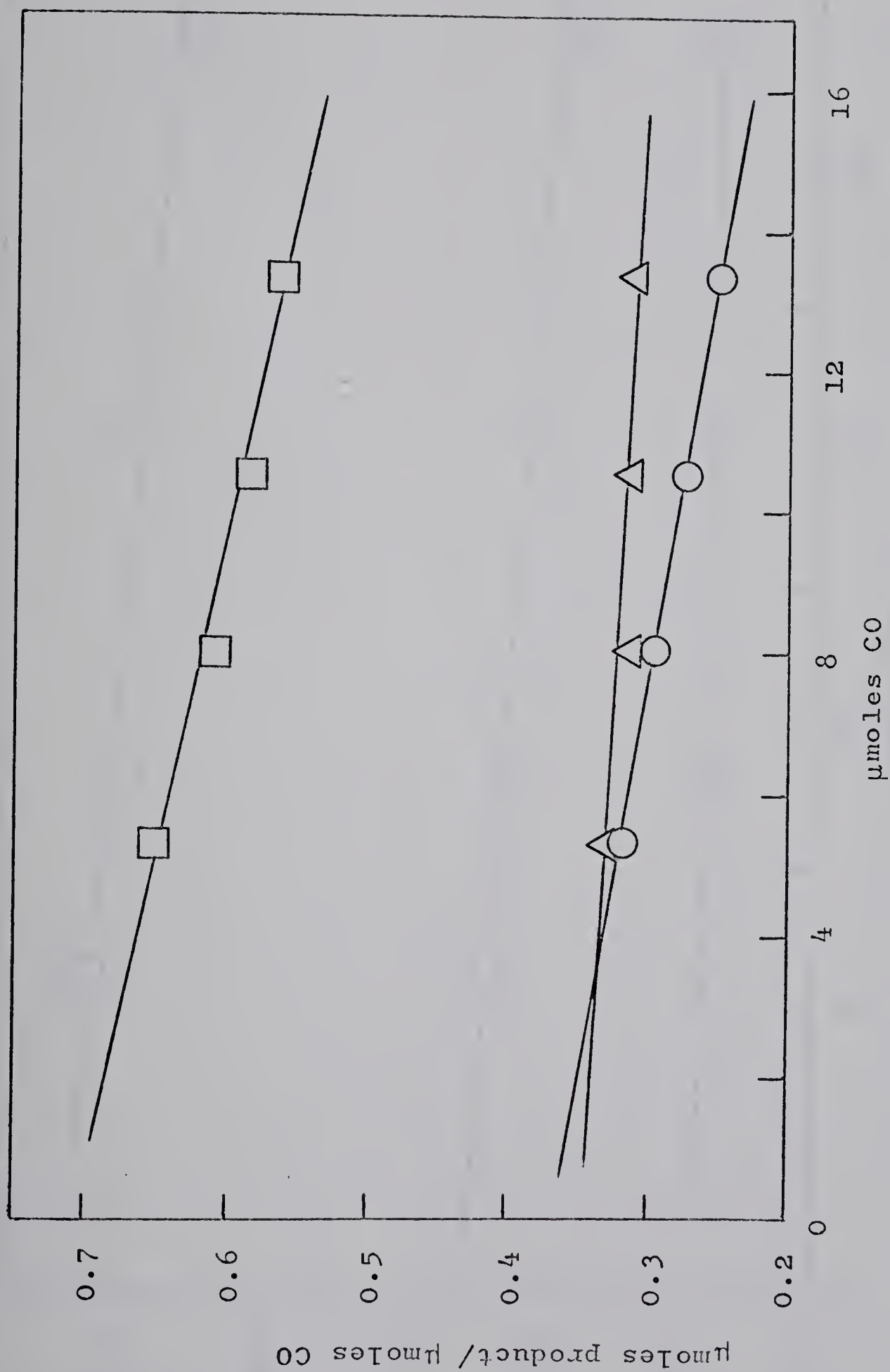


Fig. 6 Rates of product formation as a function of CO yield in the  $\text{COS-C}_2\text{H}_4$  system for photolysis by med. pressure Hg arc. ○ = vinyl mercaptan; △ = ethylene episulfide; □ = vinyl mercaptan + ethylene episulfide





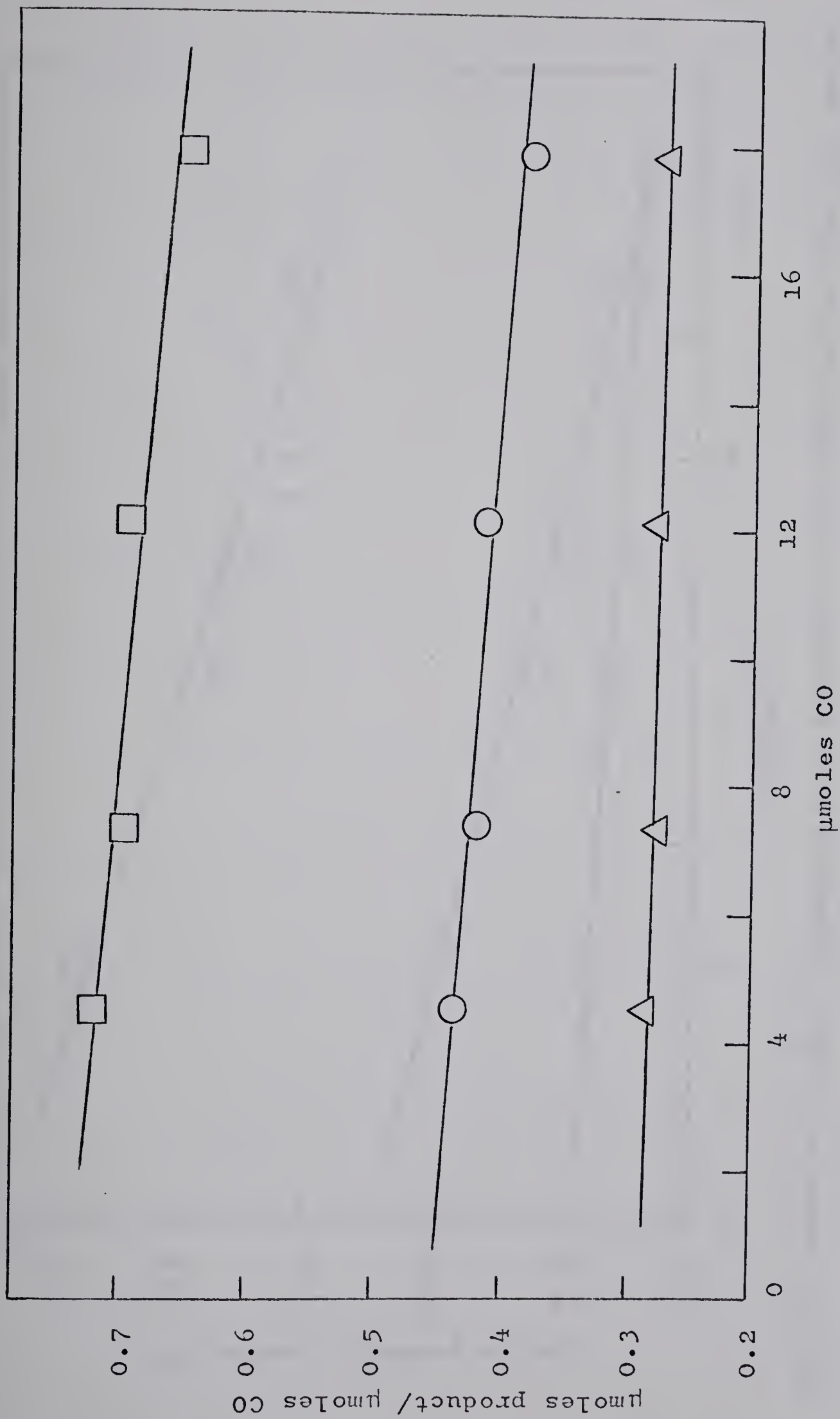


Fig. 7 Rates of product formation as a function of CO yield in the  $\text{COS-C}_2\text{H}_4$  system for photolysis by Cd lamp.  $\circ$  = vinyl mercaptan;  $\triangle$  = ethylene episulfide;

$\square$  = vinyl mercaptan + ethylene episulfide



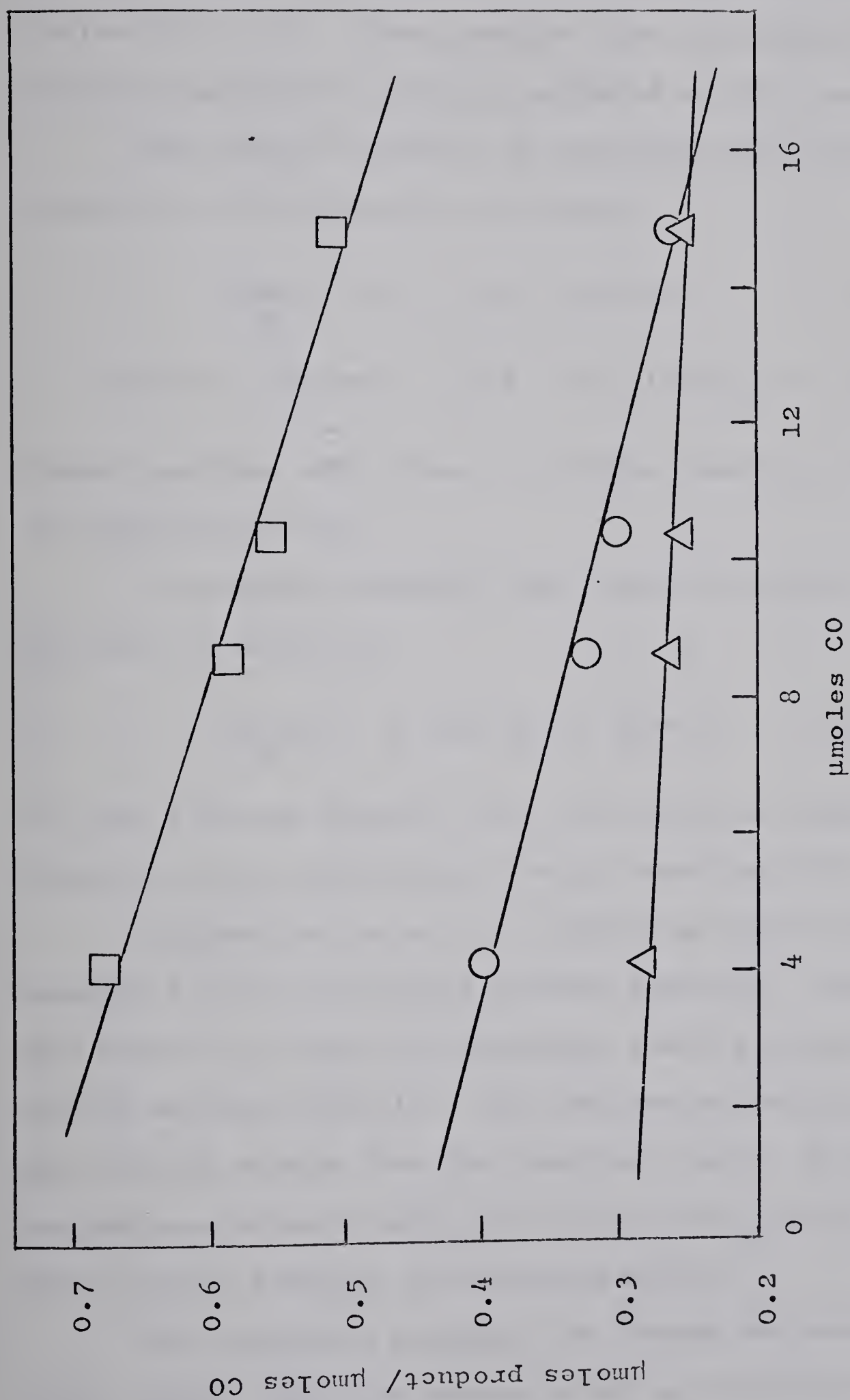
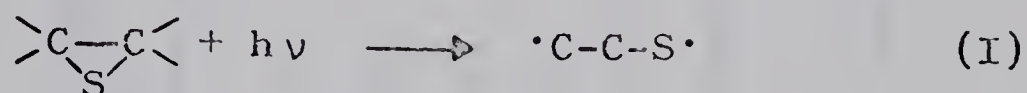


Fig. 8 Rates of product formation as a function of CO yield in the  $\text{COS-C}_2\text{H}_4$  system for photolysis by Zn lamp. ○ = vinyl mercaptan; △ = ethylene episulfide; □ = vinyl mercaptan + ethylene episulfide



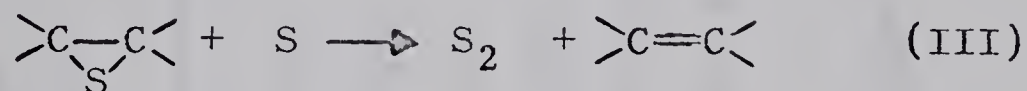
was also observed in several other olefin systems as shown in Tables XVII - XX. These studies also illustrate that the sulfur-compounds are primary products of the reaction.

The loss of products by secondary photolysis may result from the following reactions:



These reactions were shown to proceed readily in the photolysis of episulfides (97).

A secondary reaction that would contribute to the decrease in yields is:



For the 1-butene system, this step has been shown to be much faster than the episulfide forming reaction (69).

Polymerization of the vinylic mercaptans would also account for the incomplete product recovery. These compounds are known to be reactive monomers, readily polymerizing on active surfaces (72,81). The non-terminal vinylic mercaptans may be less stable than the terminal isomers and their conspicuous absence among the products may be related to their strong tendency for polymerization.

The mercaptan products are formed exclusively from  $\text{S}(^1\text{D})$  atoms. This was demonstrated by experiments employing





TABLE XVII

RATES OF PRODUCT FORMATION AS A FUNCTION OF TIME IN THE COS C<sub>3</sub>H<sub>6</sub> SYSTEM<sup>a</sup>

Time, min.	Rates, $\mu\text{moles/min.} \times 10$						
	CO	AM <sup>b</sup>	MVM <sup>b</sup>	PS <sup>b</sup>	$\Sigma R(\text{AM, MVM, PS})$	$\frac{\Sigma R(\text{AM, MVM})}{R(\text{PS})}$	$\frac{\Sigma R(\text{AM, MVM, PS})}{R(\text{CO})}$
10	1.02	0.095	0.104	0.533	0.73	0.37	0.72
20	1.29	0.106	0.104	0.494	0.70	0.43	0.54
40	1.36	0.091	0.090	0.441	0.62	0.41	0.46
60	1.36	0.084	0.077	0.423	0.58	0.38	0.43

<sup>a</sup>P(COS) = 100 torr; P(C<sub>3</sub>H<sub>6</sub>) = 200 torr; light source, med. pressure Hg arc;  
incident intensity variable

<sup>b</sup>AM = allyl mercaptan; MVM = cis + trans-propene-1-thiol; PS = propylene episulfide



TABLE XVIII

RATES OF PRODUCT FORMATION AS A FUNCTION OF TIME IN THE COS-CF<sub>2</sub>CH<sub>2</sub> SYSTEM<sup>a</sup>

Time, min.	Rates, $\mu\text{moles/min.} \times 10$				
	CO	DFVM <sup>b</sup>	DFES <sup>b</sup>	$\Sigma R(\text{DFVM}, \text{DFES})$	$\frac{R(\text{DFVM})}{R(\text{DFES})} \quad \frac{\Sigma R(\text{DFVM}, \text{DFES})}{R(\text{CO})}$
15	2.45	0.45	1.06	1.51	0.42      0.62
45	2.40	0.30	0.90	1.20	0.33      0.50
60	2.36	0.26	0.86	1.12	0.30      0.47

<sup>a</sup>P(COS) = 100 torr; P(CF<sub>2</sub>CH<sub>2</sub>) = 400 torr; light source, med. pressure Hg arc

<sup>b</sup>DFVM = 2,2-difluorovinyl mercaptan; DFES = 1,1-difluoroethylene episulfide



TABLE XIX

## RATES OF PRODUCT FORMATION AS A FUNCTION OF TIME

IN THE COS-trans-1,2-CFHCFH SYSTEM<sup>a</sup>

Time, min.	Rates, $\mu\text{moles/min.} \times 10^{-4}$				
	CO	$\frac{\text{trans-1,2-DFES}^b}{\text{DFES}}$	$\frac{\text{cis-1,2-DFES}}{\text{DFES}}$	$\frac{\Sigma R(\text{trans+cis-1,2-DFES})}{R(\text{cis-1,2-DFES})}$	$\frac{\Sigma R(\frac{\text{trans+cis-1,2-DFES}}{1,2\text{-DFES}})}{R(\text{CO})}$
30	0.77	0.23	0.053	0.28	4.34
60	0.74	0.23	0.053	0.28	4.34
90	0.71	0.22	0.048	0.27	4.58
120	0.69	0.21	0.047	0.26	4.47
150	0.67	0.20	0.044	0.24	4.54
					0.36
					0.38
					0.38
					0.37
					0.36

<sup>a</sup>P(COS) = 100 torr; P(trans-1,2-CFHCFH) = 400 torr; light source, Cd spectral lamp<sup>b</sup>DFES = difluoroethylene episulfide





TABLE XX

## RATES OF PRODUCT FORMATION AS A FUNCTION OF TIME

IN THE COS-C<sub>2</sub>F<sub>3</sub>H SYSTEM<sup>a</sup>

Time, min.	Rates, $\mu\text{moles/min.} \times 10$			$\frac{R(\text{TFES})}{R(\text{CO})}$
	CO	TFES <sup>b</sup>	CS <sub>2</sub>	
15	0.99	0.27	0.03	0.27
30	0.91	0.23	0.01	0.25
40	0.93	0.21	0.01	0.23
50	0.91	0.22	0.01	0.24
60	0.87	0.21	0.01	0.24

<sup>a</sup>p(COS) = 100 torr; P(C<sub>2</sub>F<sub>3</sub>H) = 750 torr; light source, Cd spectral lamp<sup>b</sup>TFES = trifluoroethylene episulfide

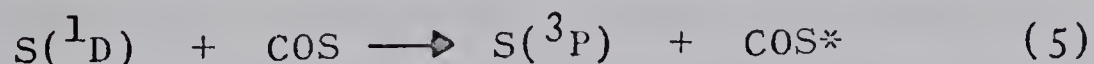


the mercury sensitization of COS to produce triplet sulfur atoms (69). These formed only episulfides in reactions with olefins. Mercaptans were not observed with either olefins or paraffins. Hence mercaptans arise only from  $S(^1D)$  atoms, while episulfides may be formed from both  $S(^1D)$  and  $S(^3P)$  atoms. From comparisons of the relative rate constants for  $S(^3P)$  and  $S(^1D)$  additions to olefins, it has been estimated that more than 70% of the episulfides are formed from singlet atoms in the COS-olefin systems (70).

The pressure dependence exhibited by the ratio  $R(\text{mercaptan})/R(\text{episulfide})$  may then be due to a change in the singlet-to triplet-atom distribution. A larger collisional stabilization requirement on the initially formed "hot" mercaptan would also contribute to this effect.

While a small pressure stabilization was observed for vinyl mercaptan from the ethylene reaction (69), this factor is not important for the  $C_4$ -olefins where product recoveries were large (95 - 97%). This indicates that little or no decomposition of "hot" molecules occurs at low olefin pressures.

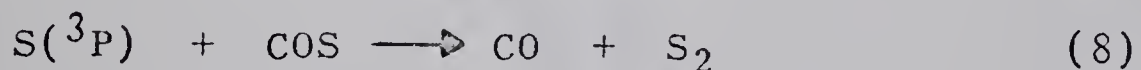
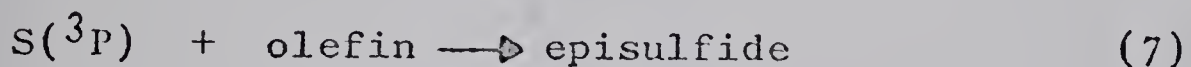
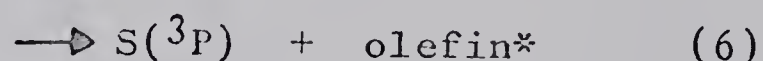
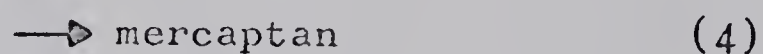
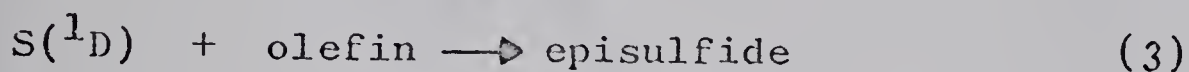
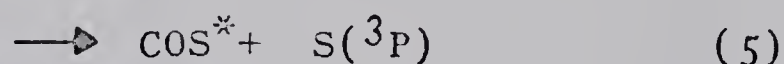
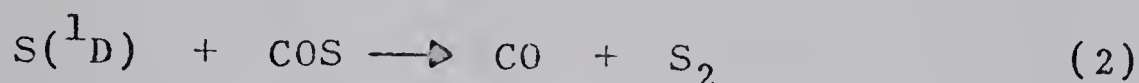
At low olefin pressures  $S(^3P)$  atoms may be formed via an efficient electronic deactivation of singlet sulfur atoms by COS,





The deactivation of  $S(^1D)$  atoms by the olefin, by analogy with the paraffin systems (64), may also contribute triplet sulfur atoms to the olefin-COS systems.

The general scheme for the COS-olefin systems may then be represented by the following sequence of reactions:



Triplet sulfur atoms have been shown to react much faster with olefins than with COS (80), and if step 8 is set to zero, a stationary state treatment gives the following expression:

$$\frac{R^0(\text{CO})/2}{R(\text{CO}) - R^0(\text{CO})/2} = \frac{k_2 + k_5}{k_2} + \frac{(O1)}{(\text{COS})} \cdot \frac{k_3 + k_4 + k_6}{k_2} \quad (\text{IV})$$

Plots of equation IV for small  $(O1)/(\text{COS})$  ratios are shown in Figs. 9 and 10 for ethylene, propylene, cis-1,2-difluoroethylene and trifluoroethylene. Values obtained for the expression at higher ratios of  $(O1)/(\text{COS})$  showed large



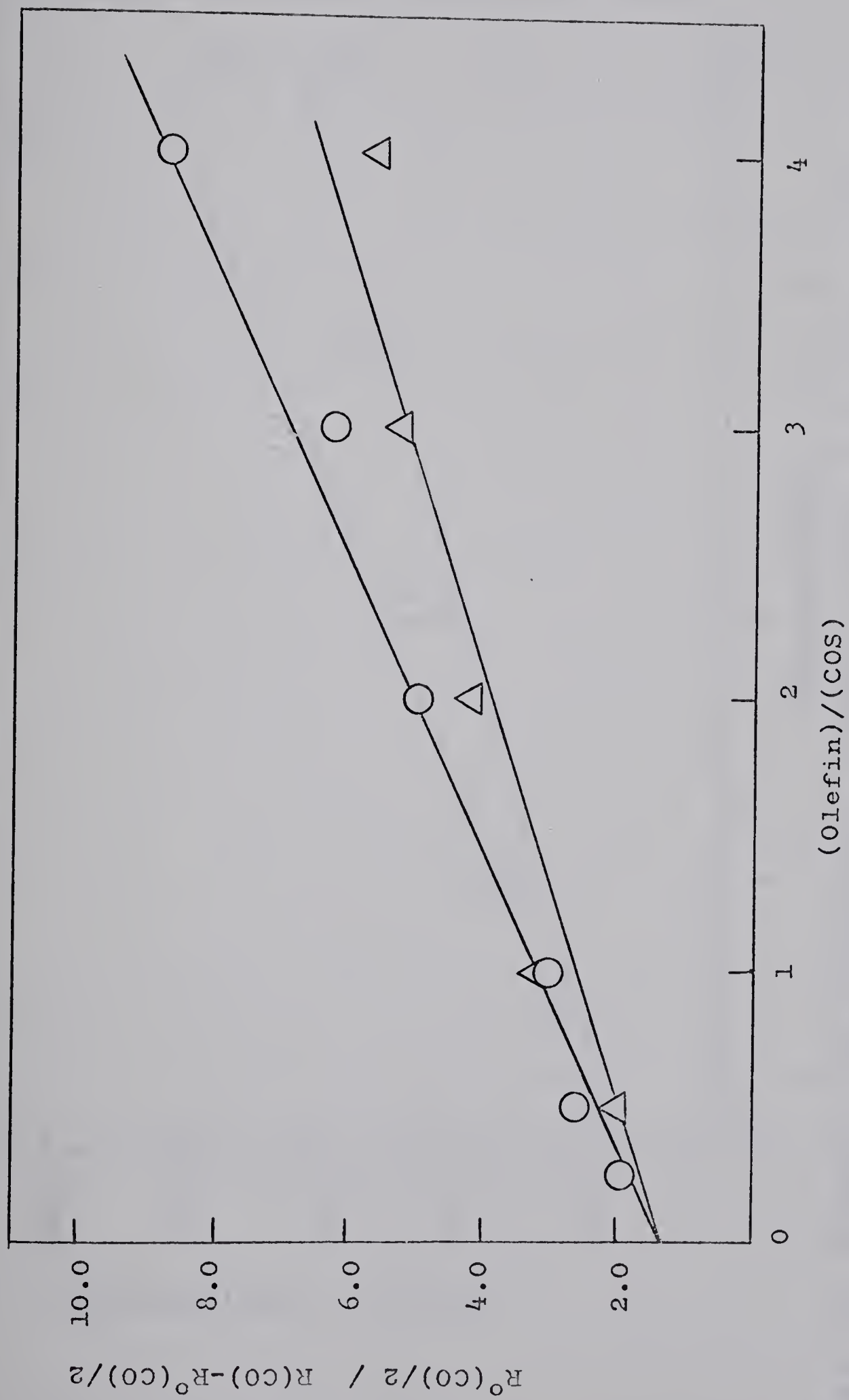


Fig. 9  $R^O(CO)/2 / R(CO)-R^O(CO)/2$  vs.  $(Olefin)/(CO)$  for ethylene ( $\circ$ ) and cis-1,2-difluoroethylene ( $\triangle$ ).





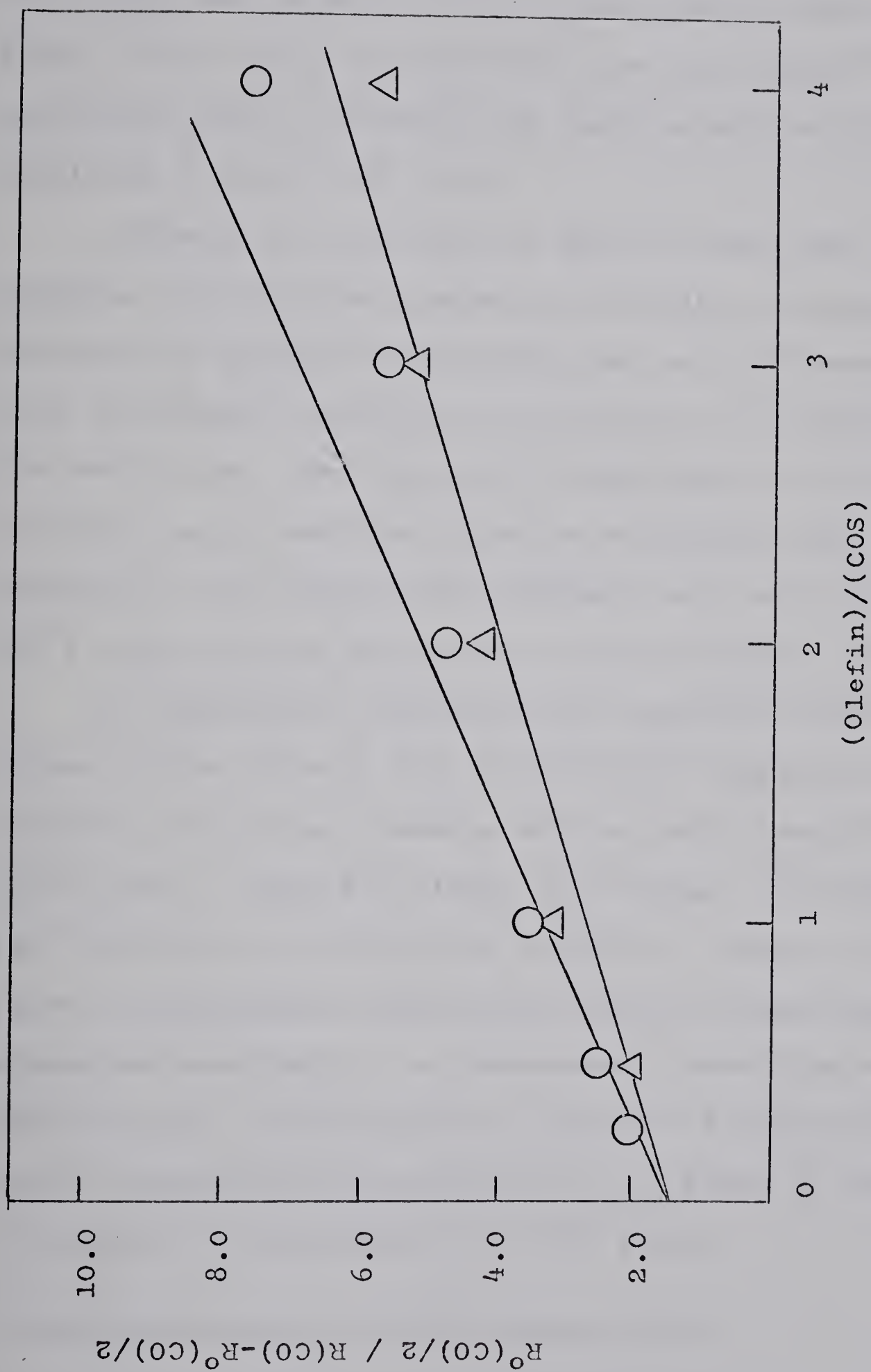


Fig. 10  $R^\circ(\text{CO})/2 / R(\text{CO}) - R^\circ(\text{CO})/2$  vs.  $(\text{Olefin})/(\text{CO})$  for propylene (O) and trifluoroethylene ( $\Delta$ ).



deviations and probably reflect experimental error. At larger ratio values of  $(O_1)/(COS)$  the term  $R(CO)-R^O(CO)/2$  approaches that of  $R^O(CO)/2$  and small errors are greatly magnified in the L.H.S. term.

Although the data seem to give a linear plot for the ethylene and propylene systems, a definite curvature is observed for cis-1,2-difluoroethylene and trifluoroethylene. This is probably related to the exclusion of reaction 8 in the derivation. This step may be important in the low pressure region and thus cannot be eliminated from the mechanism, since fluorinated olefins react much slower with  $S(^3P)$  atoms than do hydrocarbon olefins (Chapter VI).

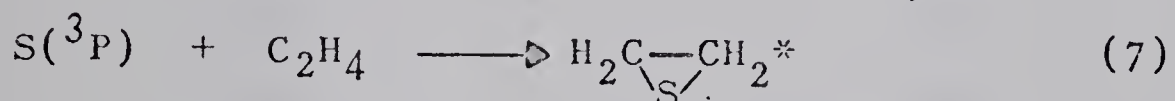
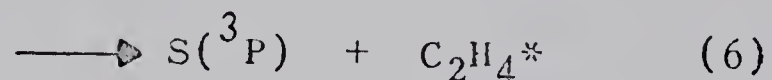
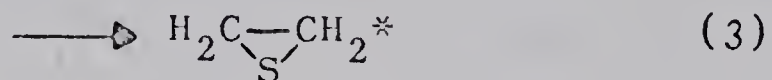
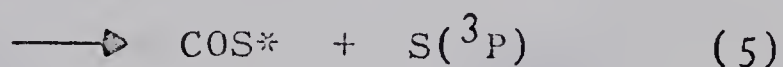
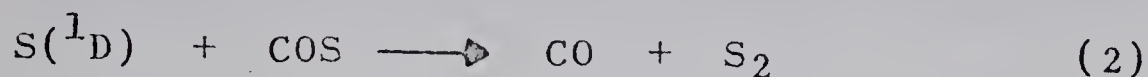
If equation IV represents the reaction kinetics, the slopes of the plots in Fig. 9 and 10 for ethylene and propylene should be a measure of the olefin reactivity with  $S(^1D)$  atoms. Since the slopes are similar, it would appear that both olefins are equally reactive. However, the large degree of uncertainty associated with the slopes makes the comparison unreliable. An independent investigation (70), measuring the relative product yields in a competitive system, indicated that propylene is 2.9 times as reactive as ethylene in reactions with  $S(^1D)$  atoms.

### 3) The deactivation of $S(^1D)$ atoms by COS

A study of the product ratio of ethylene episulfide to vinyl mercaptan as a function of the concentration ratio



$(\text{COS})/(\text{C}_2\text{H}_4)$  was utilized to estimate the importance of the deactivation of  $\text{S}(^1\text{D})$  atoms by COS. From Table XXI and Fig. 11 it is seen that the relation is linear and can be interpreted by the following sequence of competing reactions:



Triplet sulfur atoms react much faster with olefins than with COS (80) and at moderately high values of  $(\text{COS})/(\text{C}_2\text{H}_4)$  the predominant reaction of  $\text{S}(^3\text{P})$  atoms is step 7. With this assumption a stationary state treatment of reactions 2 - 7 leads to the equation

$$\text{R(ES)}/\text{R(VM)} = (k_3 + k_6)/k_4 + (k_5/k_4) \cdot (\text{COS})/(\text{C}_2\text{H}_4) \quad (\text{V})$$

Combining these results with those obtained from equation IV for the ethylene system, gives the relative rate ratio for the abstraction and deactivation reactions of  $\text{S}(^1\text{D})$  with COS as  $k_2/k_5 = 3.8$ .





TABLE XXI

RELATIVE RATES OF VINYL MERCAPTAN  
AND ETHYLENE EPISULFIDE FORMATION AS A FUNCTION  
OF ADDED COS PRESSURE IN THE COS-C<sub>2</sub>H<sub>4</sub> SYSTEM<sup>a</sup>

$\frac{P(\text{COS}), \text{torr}}{P(\text{C}_2\text{H}_4), \text{torr}}$	$\frac{R(\text{ES})}{R(\text{VM})}$ <sup>b</sup>
0.25 <sup>c</sup>	1.1
0.50 <sup>c</sup>	1.2
1.00	1.3
2.00	1.5
3.00	1.8
4.00	2.1
5.00	2.5
6.00	2.7
7.00	3.0
8.00	3.3
9.00	3.7

<sup>a</sup>P(C<sub>2</sub>H<sub>4</sub>) = 100 torr; exposure time = 20 min.; photolysis  
by med. pressure Hg arc

<sup>b</sup>VM = vinyl mercaptan; ES = ethylene episulfide

<sup>c</sup>pressure stabilization region, i.e. P > 300 torr



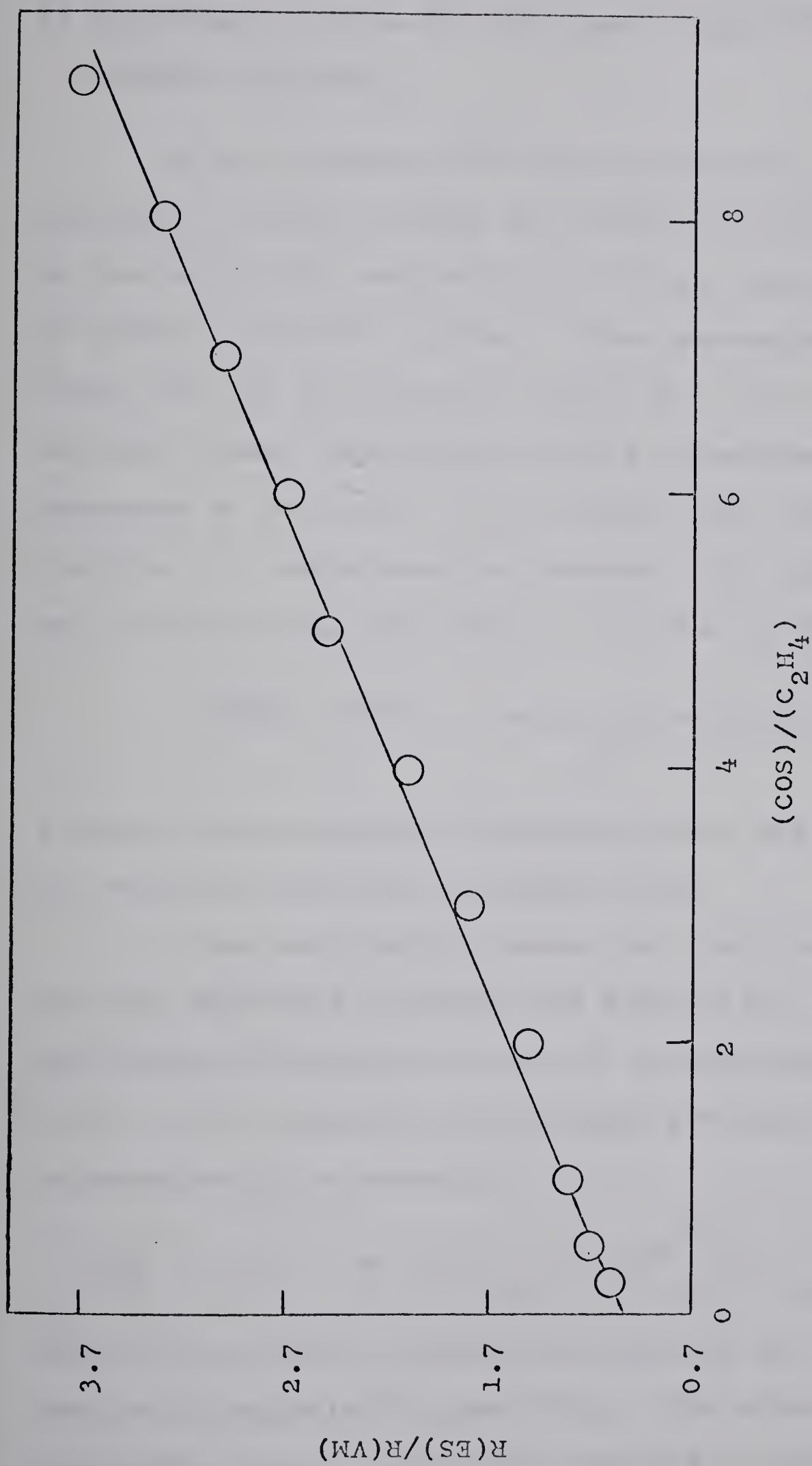
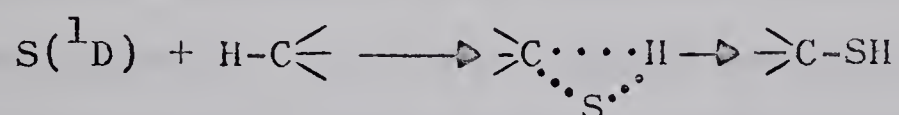


Fig. 11  $R(ES)/R(VM)$  vs.  $(COS)/(C_2H_4)$  for the COS-ethylene system.



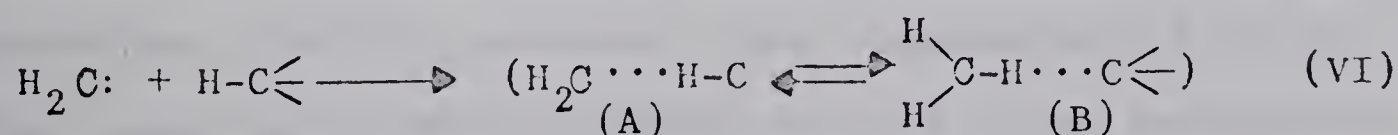
4) Transition complex for the reaction of S(<sup>1</sup>D) atoms with alkenyl C-H bonds

In the 1-butene-S(<sup>1</sup>D) atom system the alkenyl mercaptan products, 1-butene-3-thiol and 1-butene-4-thiol, were obtained in the ratio 2:3, indicative that these compounds are formed by random insertive attack. Since mercaptans and episulfides were the only products observed in experiments of short exposure times, abstraction and the subsequent recombination processes do not occur. This implies that the insertion reaction is a rapid one-step process, with simultaneous C-S and S-H bond formation during the attack on the C-H bond:



A similar three-membered transition state has been proposed for methylene insertion reactions (13).

A less acceptable proposal for the insertion mechanism has been described by DeMore and Benson (3). It was suggested that attack by methylene occurs on the hydrogen atom, since attack on the electrons of the small C-H bond is expected to be structurally unfavorable

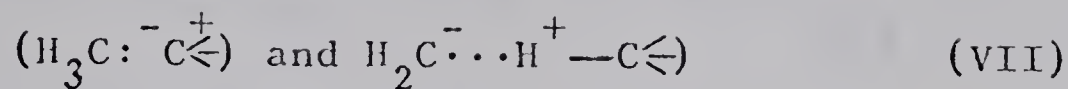


Adduct B is viewed as being equivalent to the recombination complex of radicals  $CH_3\cdot$  and  $\cdot C\leq$ . The attractive potential between the loosely associated radicals is attributed to





partial contribution of ionic states such as:



Accordingly, rotation of these radicals into a position favoring orbital overlap would result in bond formation and account for the insertion product. On the other hand, it is also probable that the excited adduct B will fall apart into radicals, the overall result being an abstraction process. Hence insertion and abstraction processes may occur for both singlet and triplet methylene, since adduct B may be formed from either. If this were so, excess energy in the reagent should favor abstraction over insertion, since the probability of fragmentation for the "hot" adduct molecules into radicals should increase with excess energy. This is contrary to findings where the higher energy singlet methylene undergoes insertion, and the less energetic triplet species abstracts a hydrogen atom from C-H bonds (78). Insertion by triplet methylene has been proposed (79) but conclusive evidence has not yet been obtained.

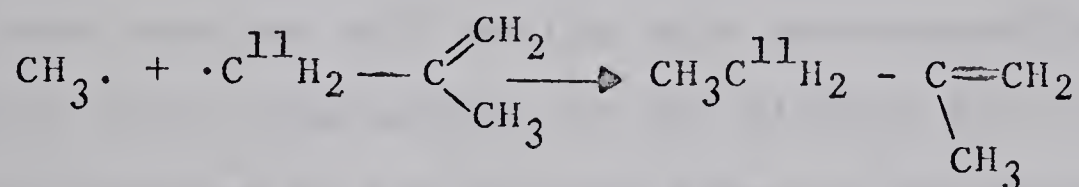
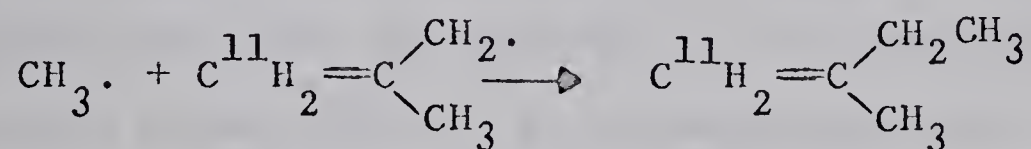
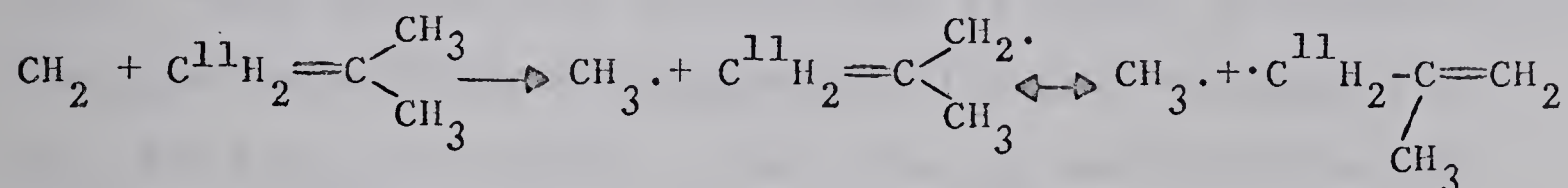
Doering and Prinzbach (98) have obtained important evidence that the insertion by singlet methylene does not proceed by a radical process. They demonstrated that the alkyl insertion product 2-methylbutene-1, from isobutylene labeled with  $\text{C}^{11}$  in the 1-position, retained a labeled carbon in the 1-position when the reaction was carried out in the liquid phase:







If the reaction had proceeded by a radical reaction scheme, scrambling should have been observed:



In the gas phase, up to 8% of the labeled carbon appeared in the 3-position, indicating direct addition as the major process, being complicated to a small extent by a radical process.

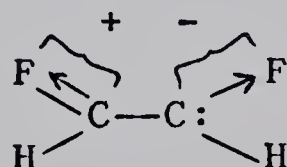
##### 5) Transition complex for the reaction of S(<sup>1</sup>D) atoms with the double bond

The formation of episulfides from S(<sup>1</sup>D) atoms and olefins may arise by addition to the double bond in a single-step insertion process resulting in simultaneous bond formation to both olefinic carbon atoms. This view was adopted by Skell and Woodward (16,77) for the reaction of methylene with double bonds in order to explain the observed



stereospecificity of singlet additions. If an intermediate biradical were formed, rotation about a C-C bond would lead to a non-stereospecific process.

Thus the reaction of 1,2-difluoroethylene with  $S(^1D)$  atoms, which yields only episulfides, is highly stereospecific. The cis-olefin yields 99% cis-episulfide and the trans-olefin over 80% trans-episulfide. Since the cis configuration for 1,2-dichloroethylene and probably 1,2-difluoroethylene is the more stable isomer (86), it is expected that the cis-olefin- $S(^1D)$  atom reaction will be the more stereospecific. The stability of the cis-isomers of the olefins may be attributed to unlike charges on the halogen atoms in mesomeric structures such as

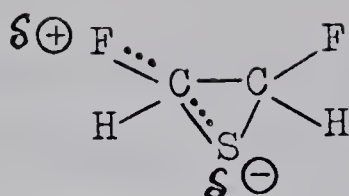


The arrow indicates polarization of the  $\sigma$ -bond.

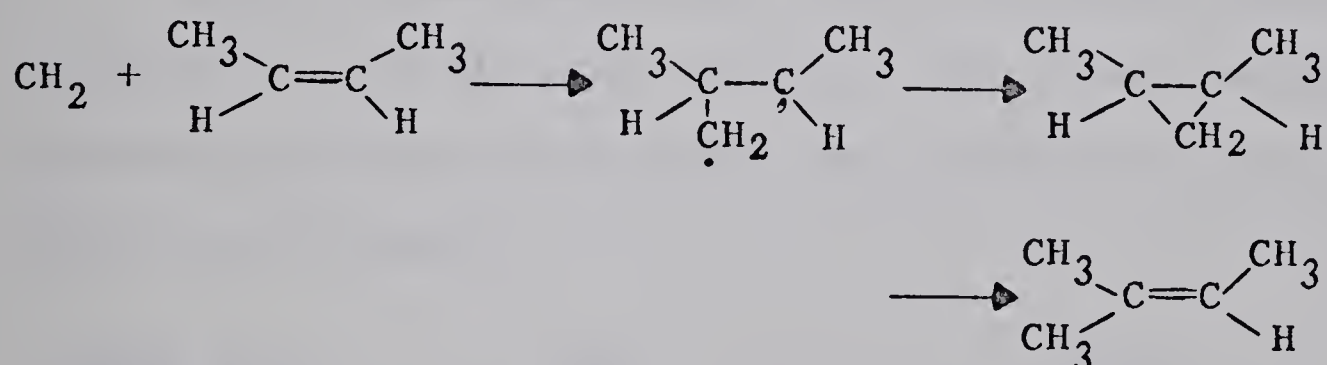
However, the trans-1,2-dichloroethylene- $S(^1D)$  reaction (70) is more stereospecific than that of the cis-isomer, and may indicate that energy inversion for the geometrical isomers of the episulfides only occurs in the fluorinated compound. Since F atoms have a high electronegativity and tend to participate in double bond formation, the lower energy of cis isomer may arise from stabilization by a structure such as:







DeMore and Benson have suggested that the mechanism for addition of singlet methylene to double bonds must include the initial formation of an energetic singlet-biradical (3). Thus for the reaction of singlet methylene with cis-2-butene, the initially formed biradical may undergo ring closure to form 1,2-dimethylcyclopropane or structural isomerization which leads to apparent insertion products:



The retention of configuration in the 1,2-dimethylcyclopropane would only depend on the competition between ring closure and rotation about the C-C bond, and it was shown that ring closure is at least  $10^{0.8}$  times faster than rotation.

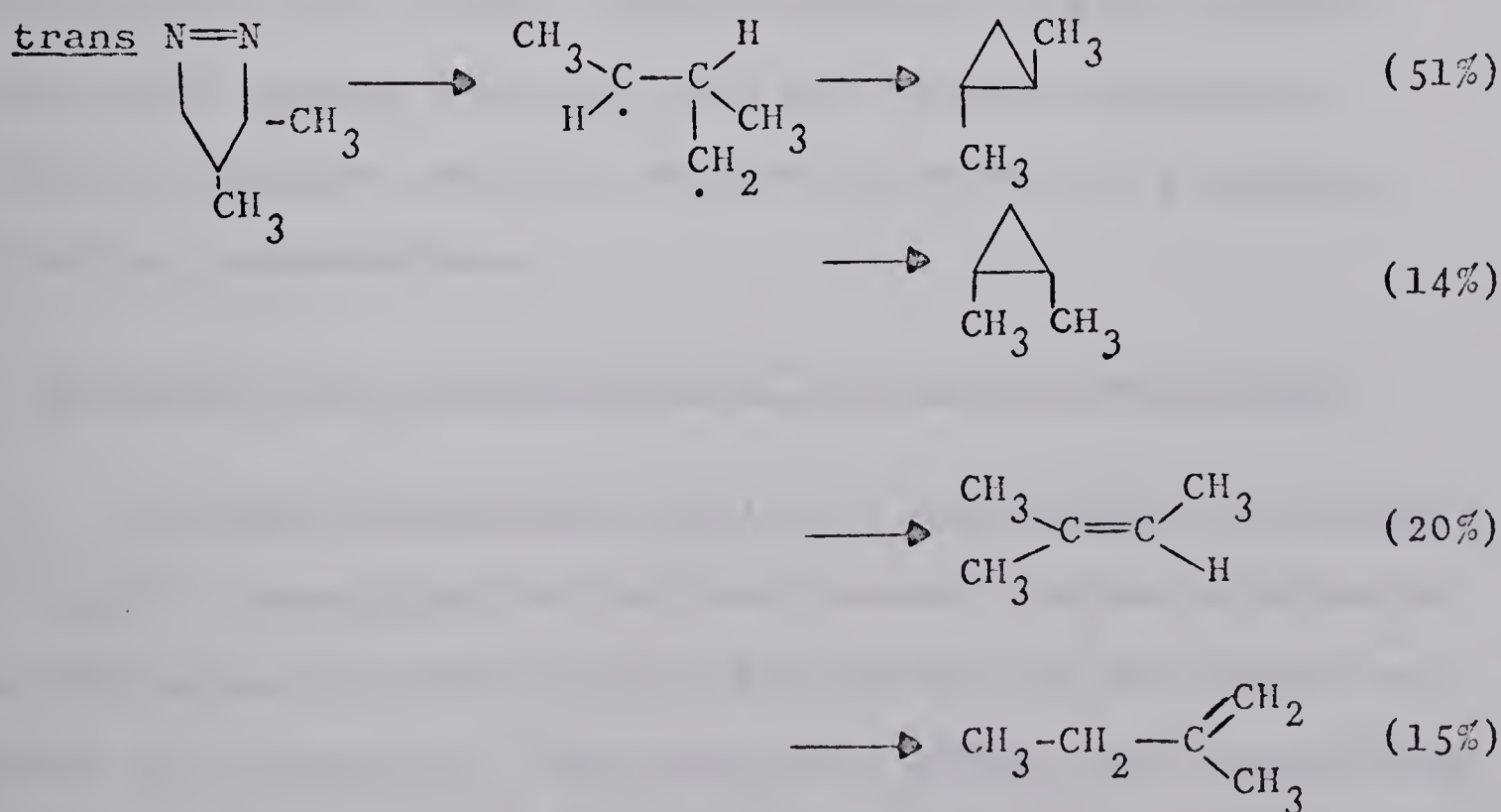
Recent evidence, however, indicates that a singlet biradical is not initially formed in singlet methylene-olefin reactions. Hoffman (99), from extended Huckel molecular orbital calculations, has constructed a potential surface for the reaction of  $\text{CH}_2(^1\text{A})$  and ethylene. He concludes that the reaction path at relatively small separation is best described





by the simultaneous formation of two new  $\sigma$ -bonds. Further evidence, that a singlet biradical may not be involved in the methylene addition reaction, was obtained from the photolysis of cis and trans- 3,4-dimethyl-1-pyrazoline (82). This system should yield the same intermediate biradical that Benson proposes for singlet methylene addition to cis or trans-2-butene. If Benson's suggestion is correct, the same products should be observed in the liquid phase reactions, where complicating isomerizations of energized products are absent.

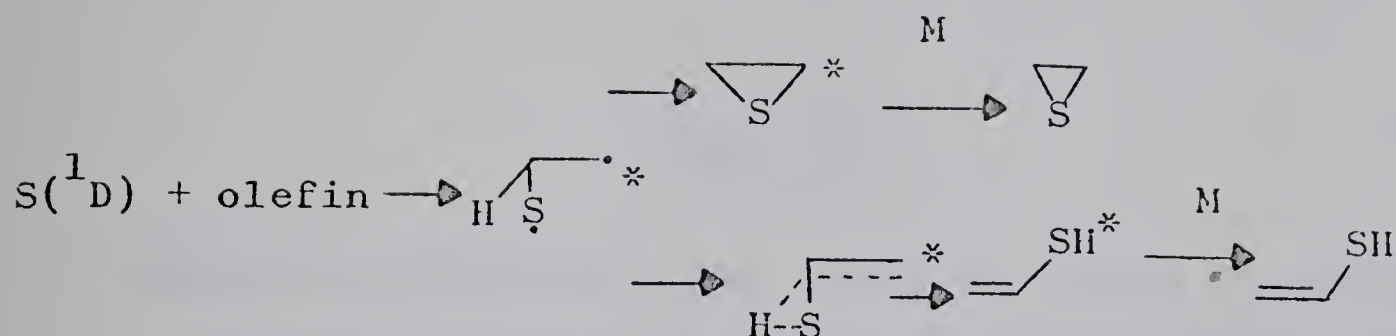
Liquid phase photolysis of the pyrazoline systems resulted in products which indicate that the biradical undergoes extensive structural and geometrical isomerization before cyclization:











While  $\text{S}({}^1\text{D})$  atom addition to double bonds of olefins, by analogy with the methylene addition reaction, probably proceeds by a concerted insertion-type process, there may be sufficient excess energy in the initially formed episulfide for ring opening. Calculations for the exothermicity of the episulfide forming reactions, Table XXII, show that 85-88 kcal./mole of excess energy is present in these products.

The dissociation energies of the C-S bonds in the episulfides are not available, but may be estimated by an indirect method as suggested by Benson for the C-C bond dissociation energy in cyclopropane (100). The estimations as shown for ethylene episulfide, involve the following cycle:



$$\Delta H_f(\cdot\text{CH}_2\text{CH}_2\text{S}\cdot) = D(\text{S-H}) + D(\text{C-H}) - 2 \Delta H_f(\text{H}) - \Delta H_f(\text{CH}_3\text{CH}_2\text{SH})$$



$$D(\text{C-S}) = \Delta H_f(\cdot\text{CH}_2\text{CH}_2\text{S}\cdot) - \Delta H_f(\text{ethylene episulfide})$$





TABLE XXII

ESTIMATED EXOTHERMICITIES, IN KILOCALORIES PER MOLE,  
 FOR THE REACTION  $S(^1D) + \text{OLEFIN} \longrightarrow \text{EPISULFIDE}^a$

Substrate	$\Delta H_f^o(\text{substr})^b$	$\Delta H_f^o(\text{episulfide})^c$	$\Delta H(\text{reaction})$
Ethylene	12.5	19.9	-84.9
Propylene	4.9	11.0	-86.3
Isobutylene	-3.2	2.7	-85.5
<u>cis</u> -2-Butene	-1.7	2.7	-88.0
<u>trans</u> -2-Butene	-2.9	0.9	-88.6

$^a\Delta H_f^o(S)$  taken as 66.0 kcal./mole, reference 67.

$E(S(^1D)) - E(S(^3P)) = 26.4$  kcal./mole.

$^b$ From reference 102.

$^c$ From reference 101.





It is assumed that the bond dissociation energy of C-H in the radical is the same as that in the parent paraffin. The C-H bond dissociation energies used for these calculations were: primary C-H = 98, secondary C-H = 94.5 and tertiary C-H = 91 kcal./mole (102).  $D(S-H)$  was taken as 88 kcal./mole (103) and  $\Delta H_f(H) = 52.1$  kcal./mole. The values for the heats of formation of the mercaptans and episulfides were taken from reference 101. The calculated C-S bond energies are shown in Table XXIII. Thus these calculations indicate that the intermediate biradicals may have about 34 kcal./mole of excitation energy which may be sufficient for the structural isomerization to the vinylic mercaptan.

If the formation of the vinylic mercaptans proceeds by the isomerization of "hot" episulfide molecules, it would be expected that ring opening would occur predominantly at the weaker C-S bond. Since the weaker C-S bond is formed at non-terminal ends of  $\alpha$  substituted episulfides, it is probable that only terminal vinylic mercaptans will be formed. This is confirmed by the results from the propylene and 1-butene systems, in which only terminal mercaptans were formed.

Vinylic mercaptans, however, were never observed with  $\alpha, \beta$  substituted olefins. An exception to this is the cyclopentene system where small yields of the vinylic mercaptan, cyclopentene-1-thiol were observed (70). The open chain non-terminal vinylic mercaptans may be unstable, and may



TABLE XXIII

ESTIMATION OF C-S BOND DISSOCIATION ENERGIES,  
IN KILOCALORIES PER MOLE, FOR EPISULFIDES<sup>a</sup>

Compound	Radical	H <sub>f</sub> (Radical)	D(C-S)
Ethylene Ep.	$\cdot\text{CH}_2\text{CH}_2\text{S}\cdot$	70.8	50.9
Propylene Ep.	$\text{CH}_3\dot{\text{C}}\text{HCH}_2\text{S}\cdot$	62.1	51.1
	$\text{CH}_3\underset{\text{S}\cdot}{\underset{ }{\text{C}}}\text{CH}_2\cdot$	63.6	52.6
<u>trans</u> -2-Butene Ep.	$\begin{array}{c} \text{CH}_3 \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} - \text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{S}\cdot \\ \quad \quad \quad \text{CH}_3 \end{array}$	54.7	53.8
<u>cis</u> -2-Butene Ep.	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{C} - \text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{S}\cdot \\ \quad \quad \quad \text{H} \end{array}$	54.7	52.0
Isobutylene Ep.	$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C} - \text{CH}_2 \\ \diagup \quad   \\ \text{CH}_3 \quad \text{S}\cdot \end{array}$	51.6	48.9
	$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C} - \dot{\text{C}}\text{H}_2 \\ \diagup \quad   \\ \text{CH}_3 \quad \text{S}\cdot \end{array}$	55.7	53.0

<sup>a</sup>The method of calculation is explained in the text.



have decomposed before analysis was completed. The large product recoveries from the cis and trans-2-butene systems indicate, however, that they are formed in trace amounts at most (69). The isomerization of energized episulfides should largely be influenced by the number of internal degrees of freedom in the molecule, and for  $\alpha$ ,  $\beta$  substituted episulfides the additional degrees of freedom may result in stabilization of the episulfide.

If vinylic mercaptans are formed by isomerization of the hot episulfide, it is expected that the isomerization would be suppressed in the condensed or solid phase. Recent data (97) showed that although the formation of vinylic mercaptans, relative to the episulfide, are reduced in the liquid and low temperature solid phases, they are still formed in significant quantities. Since these results may indicate that the vinylic mercaptans are formed by an insertion process with a relatively large activation energy, analogous reactions of  $O(^1D)$  atoms, from  $N_2O$  photolysis, were investigated. The formation of aldehydes and ketones indicated that proton shifts take place readily even in the solid phase at  $-196^\circ$ . Hence the results from the sulfur atom reactions in the liquid and solid phase need not necessarily disprove the mechanism for vinylic mercaptan formation from isomerization of hot episulfide molecules.

To explain vinylic mercaptan formation by insertion of singlet-sulfur atoms into vinylic C-H bonds requires that







severe restrictions be placed on the orientation of the attacking species. While methylene undergoes insertion into all C-H bonds of olefins (4), vinylic mercaptan formation competes favorably with insertion of  $S(^1D)$  atoms into alkyl groups only with those olefins having an unsubstituted carbon atom (Table XXIV). This suggests that a substituent group provides complete steric hindrance to vinyl C-H attack at non-terminal sites, since products arising from reactions with C-H bonds at non-terminal,  $\alpha$  substituted positions were not observed. Hence, if vinylic mercaptans are formed by an insertion process, an end-on attack on the terminal portion of the olefin leads to vinylic insertion while a similar attack at the non-terminal end leads to reactions with the substituent group. This, however, is unlikely, since  $S(^1D)$  atoms insert indiscriminately into primary, secondary and tertiary C-H bonds of paraffins (64,65).

In systems where the formation of cis and trans isomers of the vinylic mercaptan are possible, it is seen that the cis isomer formation is favored (Tables VI, IX, X). Furthermore, in the propylene-, 1-butene- and to a smaller extent in the vinyl fluoride- $S(^1D)$  atom system the ratio of the two isomers is pressure dependent. This probably indicates that energetic trans isomers are predominantly formed and unless they are collisionally stabilized, undergo geometric isomerization to the cis structure.



TABLE XXIV

A COMPARISON OF THE RELATIVE RATES  
OF VINYLIC AND ALLYLIC INSERTIONS FOR THE REACTIONS  
OF SULFUR ATOMS AND METHYLENE WITH OLEFINS<sup>a</sup>

Olefin	Vinyl H <sup>b</sup> S CH <sub>2</sub>		Allyl H S CH <sub>2</sub>	
Ethylene	0.24	0.036-0.079	...	
	0.40 <sup>c</sup>		...	
	0.39 <sup>d</sup>		...	
Propylene	0.09 <sup>e</sup>	0.03 -0.091	0.08 <sup>e</sup>	0.06-0.11
	0.11		0.11	
	0.15 <sup>c</sup>		0.14 <sup>c</sup>	
1-Butene	0.07		0.10	
Isobutylene	0.11	0.063-0.091	0.09	0.03-0.11
2-Butenes	0	0.11	0.08	0.15
Trimethylethylene	0		0.07	
Tetramethylethylene	...		0.08	
Vinyl Fluoride	0.15		...	
1,1-Difluoroethylene	0.23		...	
	0.35 <sup>c</sup>		...	
1,2-Difluoroethylene	0		...	
Trifluoroethylene	0		...	

<sup>a</sup>The data have been corrected for the statistical weight of each type of bond and are relative to double bond addition as unity. The data for methylene taken from reference 4. Photolysis is by med. pressure Hg-arc for S atoms, unless otherwise indicated.

<sup>b</sup>Insertion into non-terminal C-H bonds only observed with CH<sub>2</sub>.

<sup>c</sup>Cd lamp.      <sup>d</sup>Zn lamp.      <sup>e</sup>High intensity Hg resonance lamp.

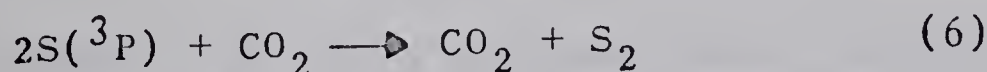
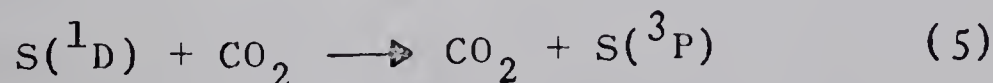
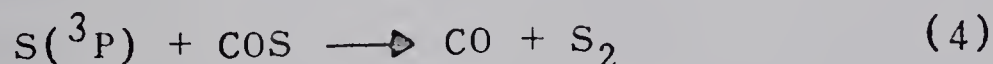
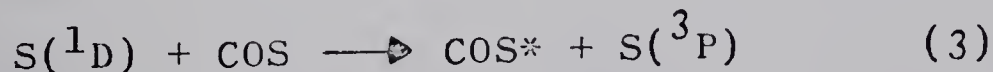
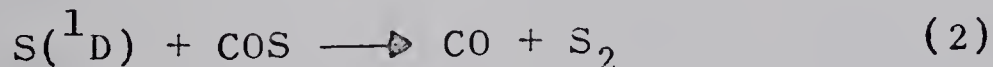
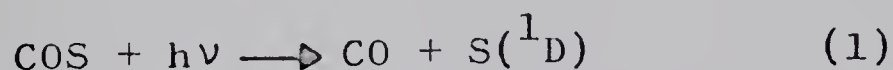


## CHAPTER V

### THE EFFECT OF INERT ("QUENCHING") GASES, WAVELENGTH OF EXCITING RADIATION, TEMPERATURE AND DEUTERATION ON THE REACTIONS OF SULFUR ATOMS WITH OLEFINS

#### 1) The effect of inert gases

When  $\text{CO}_2$  was added to 50 torr COS in increasing amounts, a continuous decrease in CO formation was observed as shown in Table XXV. Carbon dioxide has been shown to be unreactive towards sulfur atoms and only serves as an efficient deactivator of  $\text{S}(^1\text{D})$  atoms (64). The decrease in  $\text{R}(\text{CO})$  may then be attributed to third body recombination of  $\text{S}(^3\text{P})$  atoms formed by collisional deactivation of excited sulfur atoms:



The fraction of initially-formed sulfur atoms that recombine is given by the expression

$$\frac{\text{R}^0(\text{CO}) - \text{R}(\text{CO})}{\text{R}^0(\text{CO})/2}$$





TABLE XXV

RATE OF CO FORMATION AS A FUNCTION  
OF ADDED CO<sub>2</sub> PRESSURE IN THE COS SYSTEM<sup>a</sup>

P(CO <sub>2</sub> ), torr	Rates, $\mu$ moles/min. $\times 10$	
	CO	CO-CO <sup>o</sup>
0	2.52	-
50	2.49	0.03
100	2.46	0.06
200	2.42	0.10
300	2.38	0.14
400	2.34	0.18
500	2.29	0.23
600	2.28	0.24
700	2.24	0.28
800	2.19	0.33
900	2.19	0.33
1000	2.17	0.35
1100	2.11	0.41

<sup>a</sup>P(COS) = 50 torr; exposure time = 30 min;  
light source, med. pressure Hg arc





TABLE XXVI

## RATES OF PRODUCT FORMATION AS A FUNCTION

OF ADDED CO<sub>2</sub> PRESSURE IN THE COS-C<sub>3</sub>H<sub>6</sub> SYSTEM<sup>a</sup>

P(CO <sub>2</sub> ), torr	Rates, μmoles/min. X 10					$\frac{\Sigma R(\text{AM, MVM, PS})}{R(\text{PS})}$	$\frac{\Sigma R(\text{AM, MVM, PS})}{R(\text{CO})}$
	CO	AM <sup>b</sup>	MVM <sup>b</sup>	PS <sup>b</sup>	$\Sigma R(\text{AM, MVM, PS})$		
104	1.37	0.089	0.095	0.53	0.71	0.35	0.53
288	1.36	0.076	0.091	0.65	0.82	0.26	0.60
508	1.25	0.061	0.081	0.62	0.76	0.23	0.61
806	1.30	0.049	0.074	0.66	0.78	0.19	0.60
1196	1.25	0.038	0.065	0.69	0.79	0.15	0.63

<sup>a</sup>P(COS) = 100 torr; P(C<sub>3</sub>H<sub>6</sub>) = 200 torr; exposure time = 30 min.; light source, med. pressure Hg arc

<sup>b</sup>AM = allyl mercaptan; MVM = cis+trans-propene-1-thiol; PS = propylene episulfide



TABLE XXVII

## RATES OF PRODUCT FORMATION AS A FUNCTION

OF ADDED CO<sub>2</sub> PRESSURE IN THE COS-C<sub>2</sub>H<sub>3</sub>F SYSTEM<sup>a</sup>

P(CO <sub>2</sub> ), torr	Rates, μmoles/min. X 10						$\frac{\Sigma R(t_{VM}, c_{VM}, VES)}{R(CO)}$	$\frac{\Sigma R(t_{VM}, c_{VM}, VES)}{R(CO)}$
	CO	t <sub>VM</sub> <sup>b</sup>	c <sub>VM</sub> <sup>b</sup>	VES <sup>b</sup>	ΣR(t <sub>VM</sub> , c <sub>VM</sub> , VES)			
0	1.68	0.16	0.19	0.67	1.02	0.52	0.61	
300	1.61	0.12	0.15	0.76	1.03	0.36	0.64	
600	1.61	0.07	0.10	0.85	1.02	0.20	0.63	
900	1.62	0.06	0.09	0.87	1.02	0.17	0.63	
1200	1.58	0.06	0.08	0.89	1.03	0.16	0.65	
1500	1.59	0.03	0.04	0.83	0.94	0.08	0.59	

<sup>a</sup>P(COS) = 100 torr; P(C<sub>2</sub>H<sub>3</sub>F) = 400 torr; exposure time = 30 min.; light source,

med. pressure Hg arc

<sup>b</sup>t<sub>VM</sub> = trans-2-fluoroethene-1-thiol; c<sub>VM</sub> = cis-2-fluoroethene-1-thiol;

VES = fluoroethylene episulfide



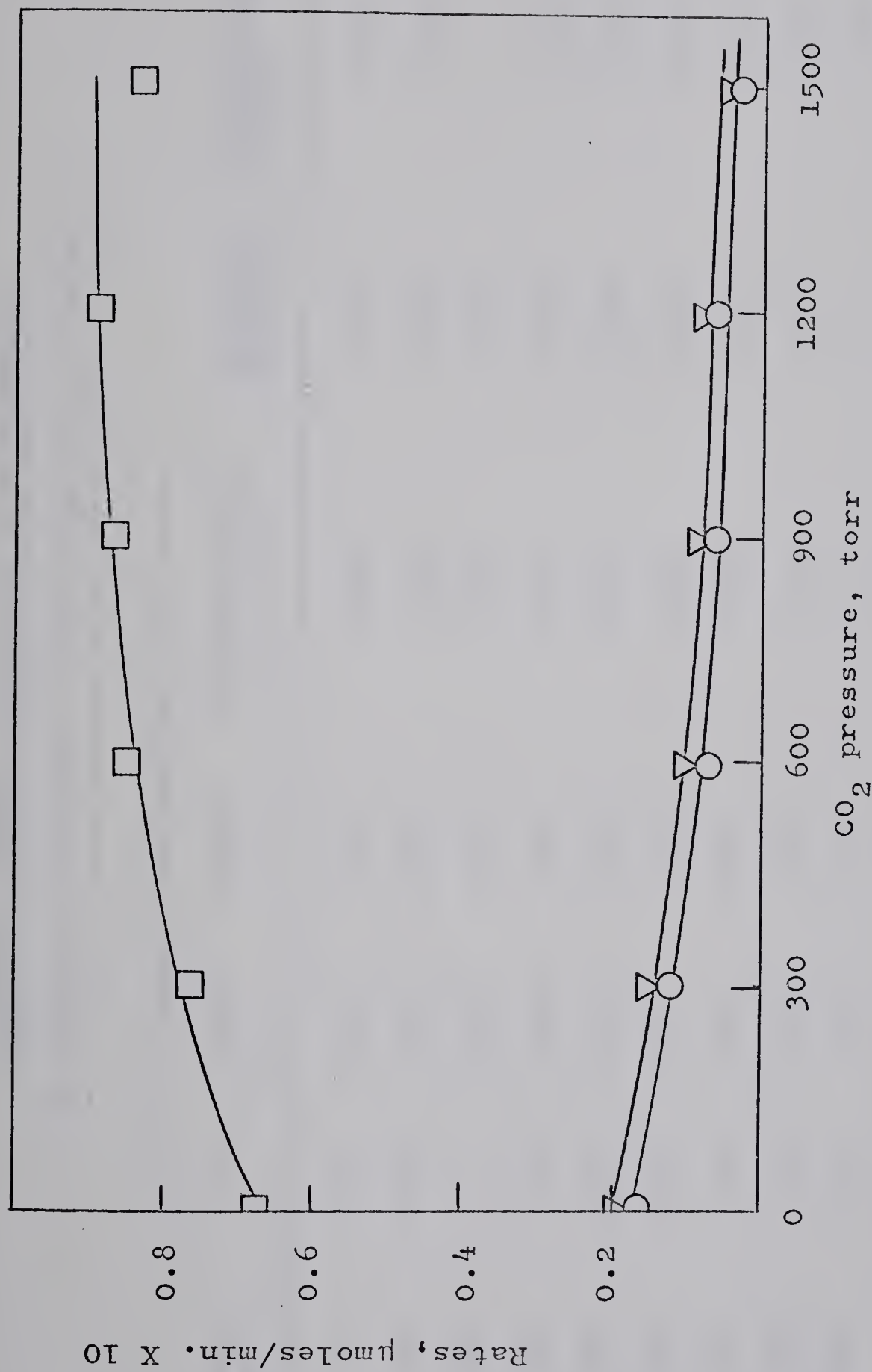


Fig. 12 Rates of product formation as a function of added  $\text{CO}_2$  pressure in the  $\text{COS-C}_2\text{H}_3\text{F}$  system.  $\bigcirc$  = trans-2-fluoroethene-1-thiol;  $\triangle$  = cis-2-fluoroethene-1-thiol;  $\square$  = fluoroethylene episulfide





TABLE XXVIII

## RATES OF PRODUCT FORMATION AS A FUNCTION

OF ADDED CO<sub>2</sub> PRESSURE IN THE COS-CF<sub>2</sub>CH<sub>2</sub> SYSTEM<sup>a</sup>

P(CO <sub>2</sub> ), torr	Rates, $\mu\text{moles/min.} \times 10$					$\frac{\Sigma R(\text{DFVM})}{R(\text{DFES})}$	$\frac{\Sigma R(\text{DFVM, DFES})}{R(\text{CO})}$
	CO	DFVM <sup>b</sup>	DFES <sup>b</sup>	$\Sigma R(\text{DFVM, DFES})$			
0	2.57	0.36	0.93	1.29	0.39	0.39	0.50
50	2.58	0.31	0.98	1.29	0.32	0.32	0.50
100	..	0.29	1.01	1.30	0.29	0.29	..
200	2.58	0.19	1.04	1.23	0.18	0.18	0.48
300	2.57	0.19	0.94	1.13	0.20	0.20	0.44
400	2.56	0.17	1.23	1.40	0.14	0.14	0.55
600	2.50	0.09	0.96	1.05	0.10	0.10	0.42
800	2.43	0.03	1.11	1.14	0.02	0.02	0.47
1000	2.37	0.02	1.11	1.13	0.02	0.02	0.48

<sup>a</sup>P(COS) = 100 torr; P(CF<sub>2</sub>CH<sub>2</sub>) = 200 torr; exposure time = 15 min.; light source,

med. pressure Hg arc

<sup>b</sup>DFVM = 2,2-difluorovinyl mercaptan; DFES = 1,1-difluoroethylene episulfide



TABLE XXIX

RATES OF PRODUCT FORMATION AS A FUNCTION

OF ADDED CO<sub>2</sub> PRESSURE IN THE COS-trans-1,2-CFHCFH SYSTEM<sup>a</sup>

P(CO <sub>2</sub> ), torr	CO	Rates, μmoles/min. X 10				%recovery <sup>c</sup>
		<u>trans</u> -1,2- DFES	<u>cis</u> -1,2- DFES	ΣR( <u>trans</u> + <u>cis</u> - 1,2-DFES)	$\frac{R(\text{trans-1,2-DFES})}{R(\text{cis-1,2-DFES})}$	
0	0.77	0.23	0.053	0.28	4.3	54
250	0.76	0.31	0.063	0.37	4.9	68
500	0.78	0.34	0.073	0.41	4.6	78
750	0.74	0.36	0.080	0.44	4.5	77
1000	0.76	0.40	0.084	0.48	4.8	89
1250	0.76	0.43	0.090	0.52	4.8	95
1500	0.76	0.42	0.087	0.51	4.8	91

<sup>a</sup>p(COS) = 100 torr; P(trans-1,2-CFHCFH) = 400 torr; exposure time = 30 min.;

light source, Cd spectral lamp; R<sup>o</sup>(CO) = 1.30 (μmoles/min. X 10)

<sup>b</sup>DFES = difluoroethylene episulfide

<sup>c</sup>%recovery of condensables in terms of R<sup>o</sup>(CO) - R(CO)



TABLE XXX

## RATES OF PRODUCT FORMATION AS A FUNCTION

OF ADDED CO<sub>2</sub> PRESSURE IN THE COS-cis-1,2-CFHCFH SYSTEM<sup>a</sup>

P(CO <sub>2</sub> ), torr	Rates, $\mu\text{moles/min.} \times 10$			% recovery <sup>c</sup>
	CO	<u>cis</u> -1,2-DFES <sup>b</sup>	CO <sup>o</sup> -CO	
0	3.46	0.72	2.14	34
250	3.36	0.96	2.24	43
500	3.51	1.07	2.09	51
750	3.48	1.21	2.12	57
1000	3.44	1.28	2.16	59
1250	3.44	1.34	2.16	62
1500	3.46	1.41	2.14	66

<sup>a</sup>P(COS) = 100 torr; P(cis-1,2-CFHCFH) = 400 torr; exposure time = 15 min.;light source, Cd spectral lamp; R<sup>o</sup>(CO) = 5.60 ( $\mu\text{moles/min.} \times 10$ )<sup>b</sup>DFES = difluoroethylene episulfide; trans-1,2-DFES less than 0.1% of cis-1,2-DFES<sup>c</sup>% recovery of condensables in terms of R<sup>o</sup>(CO)-R(CO)





TABLE XXXI

RATES OF PRODUCT FORMATION AS A FUNCTION  
OF ADDED CO<sub>2</sub> PRESSURE IN THE COS-C<sub>2</sub>F<sub>3</sub>H SYSTEM<sup>a</sup>

P(CO <sub>2</sub> ), torr	Rates, μmoles/min. X 10			$\frac{R(\text{TFES})}{R(\text{CO})}$
	CO	TFES <sup>b</sup>	CS <sub>2</sub>	
0	2.20	0.47	0.02	0.21
600	2.15	0.73	0.02	0.34
900	2.09	0.90	0.02	0.43
1200	1.98	0.93	0.02	0.47
1500	1.93	1.08	0.01	0.56

<sup>a</sup>P(COS) = 100 torr; P(C<sub>2</sub>F<sub>3</sub>H) = 400 torr; exposure time - 20 min.;

light source, med. pressure Hg arc

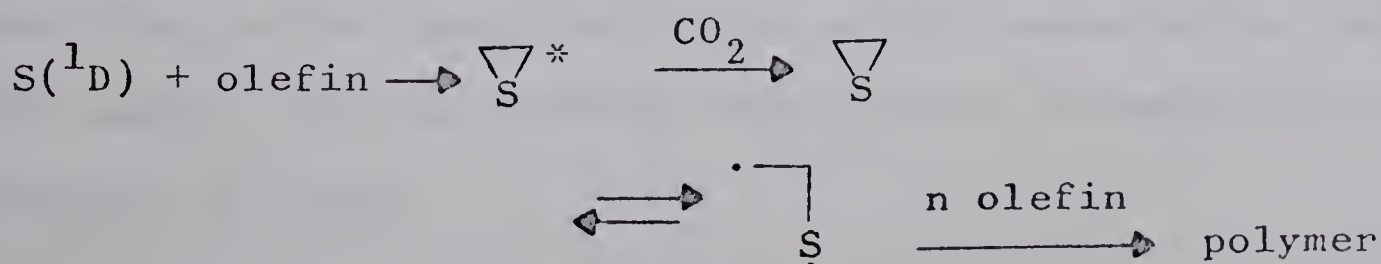
<sup>b</sup>TFES = trifluoroethylene episulfide



At 1100 torr of added  $\text{CO}_2$  and a light intensity of 0.14  $\mu\text{einstein}$ s per min., the fraction of sulfur atoms recombining was 0.33.

The effect of added  $\text{CO}_2$  to olefin-COS systems is shown in Tables XXVI - XXXI and Fig. 12. For the propylene, vinyl fluoride and 1,1-difluoroethylene systems, increasing partial pressures of  $\text{CO}_2$  resulted in a change in the isomeric product distribution. Although no effect on total product rate was observed, the mercaptan yield was suppressed at the expense of episulfide formation. Thus at higher partial pressures of  $\text{CO}_2$ , the increasing conversion of singlet sulfur atoms to  $\text{S}(^3\text{P})$ , resulted in a decrease in mercaptan formation, indicating that mercaptans arise only from the reactions of singlet sulfur atoms with olefins. Also, triplet sulfur atoms react with olefins to form only episulfides, as was seen from the concurrent increase in episulfide yield.

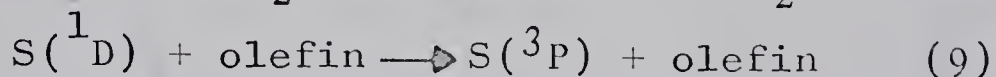
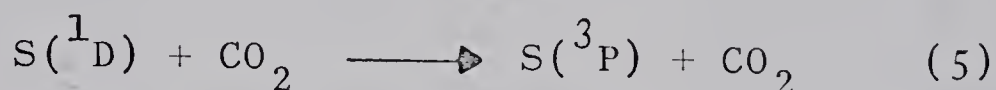
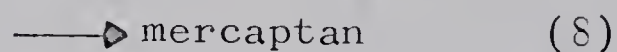
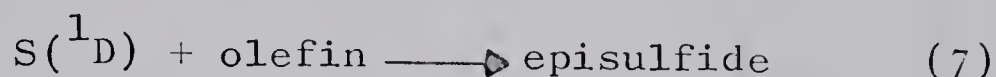
In the 1,2-difluoroethylene and trifluoroethylene systems, Tables XXIX - XXXI, the yield of episulfides showed a significant increase when the reaction was carried out in the presence of excess  $\text{CO}_2$ . The increased yield may be due to an increased stabilization of "hot" episulfide molecules and a subsequent stabilization of the ensuing polymerization processes:





The  $S(^3P)$  addition reaction is 26 kcal./mole less exothermic than that of  $S(^1D)$  atoms and added  $CO_2$  may enhance ring closure of an initially formed biradical.

For moderately high values of (olefin)/(COS), the only fate of  $S(^1D)$  atoms in the presence of  $CO_2$  is given by the following sequence of reactions:



A stationary-state treatment of the reactions gives the following expression:

$$\frac{R(\text{episulfide})}{R(\text{mercaptan})} = \frac{k_7 + k_9}{k_8} + \frac{k_5}{k_8} \frac{(CO_2)}{\text{olefin}} \quad (I)$$

Plots of equation I, using the data of Tables XXVII and XXVIII for the vinyl fluoride and 1,1-difluoroethylene systems, are linear as is shown in Fig. 13. From these results, the rate constant ratios for deactivation of  $S(^1D)$  atoms by  $CO_2$  to reaction with the olefin,  $k_5/(k_7 + k_8 + k_9)$ , are 0.7 and 0.6 for the vinyl fluoride and 1,1-difluoroethylene systems respectively.

The large deactivating efficiency of  $CO_2$  may be due to incipient bonding between singlet sulfur atoms and  $CO_2$ , resulting in the formation of an excited association complex. The complex may then undergo unimolecular decomposition to products of lower





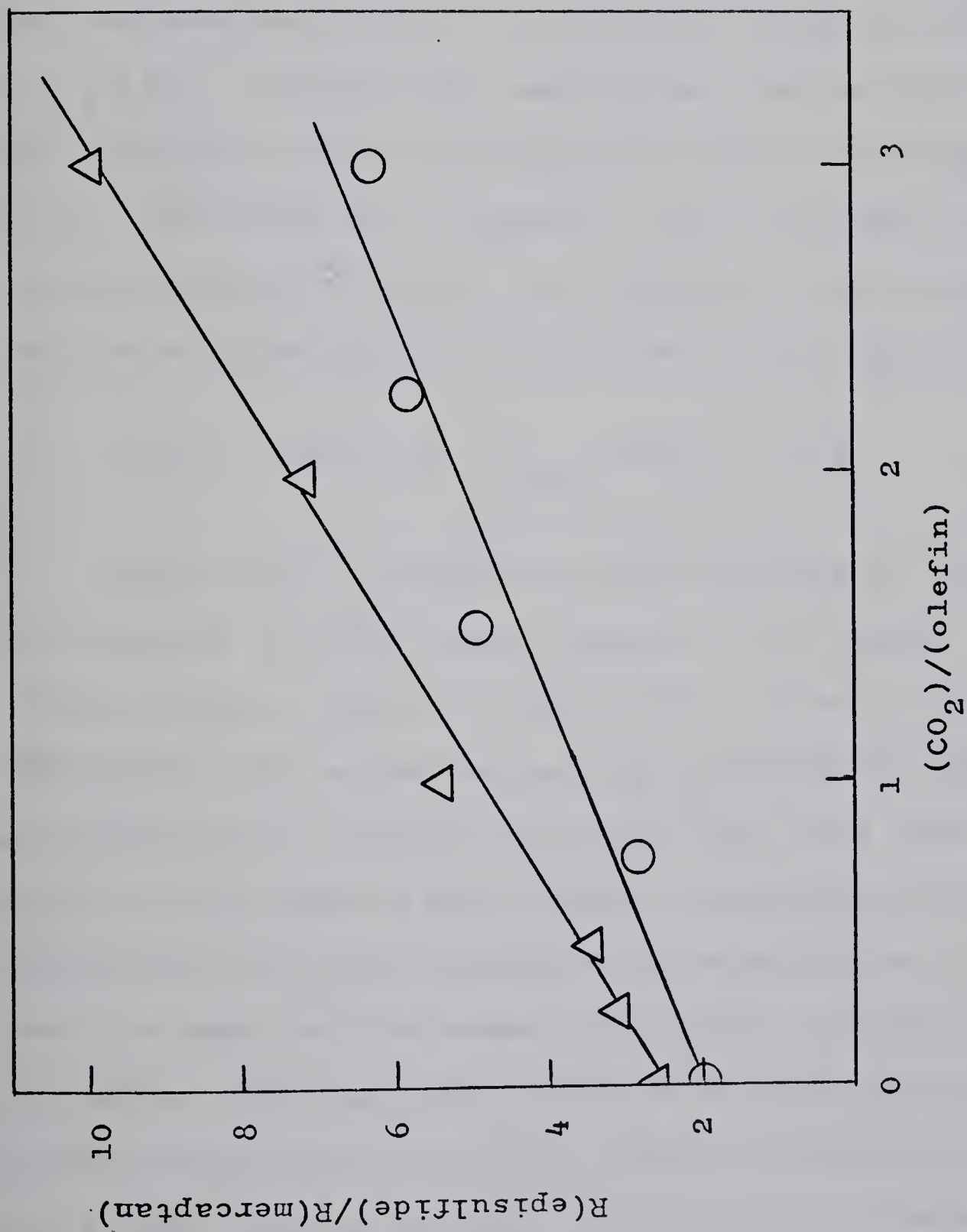
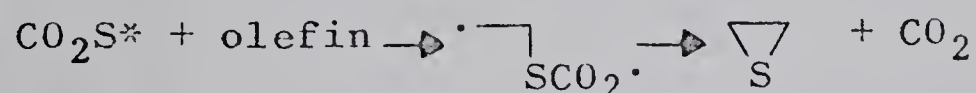


Fig. 13  $R(\text{episulfide})/R(\text{mercaptan})$  vs.  $(\text{CO}_2)/(\text{olefin})$  for the vinyl fluoride and 1,1-difluoroethylene systems. ○ = vinyl fluoride; Δ = 1,1-difluoroethylene





electronic energy in the course of stepwise vibrational deactivation. Thus the association process would facilitate spin reversal and consequently deactivate excited sulfur atoms to the ground-state triplet. Complex formation of this type has been postulated for the deactivation of  $O(^1D)$  atoms by  $CO_2$  (88). Although the association complex  $CO_3$  has never been detected, it has been suggested that it is long lived (113). Therefore, it is possible that the complex in the S-atom reaction, if formed, may undergo a rapid displacement reaction with the olefin by addition to the double bond



With Xenon, incipient chemical bonding to facilitate spin reversal of  $S(^1D)$  atoms, appears to be absent. The data for the ethylene system in Table XXXII, shows no change in  $R(VM)/R(ES)$  with increasing partial pressures of Xenon. Unfortunately the amounts of  $COS$  and  $C_2H_4$  were not well-chosen and the results may reflect a concurrent pressure stabilization of vinyl mercaptan and deactivation of sulfur atoms, as shown by the product recoveries. However, an independent study employing Xenon as an inert gas in the pressure-independent region for product formation, showed only a small initial decrease in  $R(VM)/R(ES)$  of about 5% (89). When these results are compared to those of the  $CO_2$  systems, where a continuous decrease in  $R(\text{mercaptan})/R(\text{episulfide})$  is



## RATES OF PRODUCT FORMATION AS A FUNCTION

OF ADDED XENON PRESSURE IN THE COS-C<sub>2</sub>H<sub>4</sub> SYSTEM<sup>a</sup>

P(Xe), torr	Rates, $\mu\text{moles/min.} \times 10$						$\frac{R(\text{VM})}{R(\text{ES})}$	% recovery <sup>c</sup>
	CO	VM <sup>b</sup>	ES <sup>b</sup>	$\Sigma R(\text{VM, ES})$	CO-CO			
0	1.36	0.23	0.37	0.60	0.96	0.62		63
50	1.32	0.26	0.39	0.65	1.00	0.67		65
100	1.25	0.26	0.39	0.65	1.07	0.67		61
200	1.29	0.28	0.42	0.70	1.03	0.67		68
300	1.29	0.23	0.39	0.62	1.03	0.59		69
400	1.30	0.28	0.42	0.60	1.02	0.67		72
500	1.32	0.28	0.44	0.72	1.00	0.64		75
600	1.33	0.30	0.44	0.74	0.99	0.68		67
700	1.28	0.28	0.42	0.70	1.04	0.67		72
800	1.29	0.29	0.45	0.74	1.03	0.65		75
900	1.30	0.31	0.46	0.77	1.02	0.68		75
1000	1.29	0.28	0.45	0.73	1.03	0.63		70

<sup>a</sup>P(COS) = 50 torr; P(C<sub>2</sub>H<sub>4</sub>) = 200 torr; exposure time = 30 min.; light source, med. pressure Hg arc; Ro(CO) = 2.32 ( $\mu\text{moles/min.} \times 10$ )

<sup>b</sup>VM = vinyl mercaptan; ES = ethylene episulfide

<sup>c</sup>% recovery of condensables in terms of R<sup>o</sup>(CO)-R(CO)



observed for increasing partial pressures of added  $\text{CO}_2$ , it is apparent that Xenon is an inefficient electronic deactivator of singlet sulfur atoms. Xenon, on the other hand, is a good deactivator for singlet oxygen atoms (46) and singlet methylene (22).

Carbon monoxide was also effective in collisionally deactivating singlet sulfur atoms. For the  $\text{C}_2\text{H}_4\text{-COS-CO}$  system, Table XXXIII, a continuous decrease in  $R(\text{VM})/R(\text{ES})$  was observed with increasing partial pressures of added CO. At higher partial pressures of CO, the rate of product formation is seen to increase. This indicates an increasing conversion of  $\text{S}(^1\text{D})$  atoms to the ground-state triplet, which react much faster with ethylene than with COS or CO.

Electronic deactivation of  $\text{S}(^1\text{D})$ -atoms by CO may arise from an association process in which an initial excited complex may not only redissociate to the original reactants, but also is unstable with respect to predissociation to products of lower electronic energy. As shown in Fig. 14, which schematically illustrates COS potential curves, the process may be efficient because there is the possibility of transfer from a singlet potential surface of  $\text{S}(^1\text{D})\text{-CO}$  interaction to a triplet surface of  $\text{S}(^3\text{P})\text{-CO}$  interaction.







TABLE XXXIII

RATES OF PRODUCT FORMATION AS A FUNCTION  
OF ADDED CO PRESSURE IN THE COS-C<sub>2</sub>H<sub>4</sub> SYSTEM<sup>a</sup>

P(CO), torr	Rates, $\mu\text{moles/min.} \times 10$			$\frac{R(\text{VM})}{R(\text{ES})}$
	$\text{VM}^b$	$\text{ES}^b$	$\Sigma R(\text{VM}, \text{ES})$	
0	0.26	0.25	0.51	1.04
0	0.27	0.24	0.51	1.12
200	0.24	0.31	0.55	0.78
200	0.22	0.31	0.53	0.71
400	0.21	0.47	0.68	0.45
500	0.23	0.45	0.68	0.51

<sup>a</sup> $P(\text{COS}) = 100$  torr;  $P(\text{C}_2\text{H}_4) = 200$  torr; exposure time = 30 min.;

light source, Cd spectral lamp

<sup>b</sup> $\text{VM} = \text{vinyl mercaptan}$ ;  $\text{ES} = \text{ethylene episulfide}$



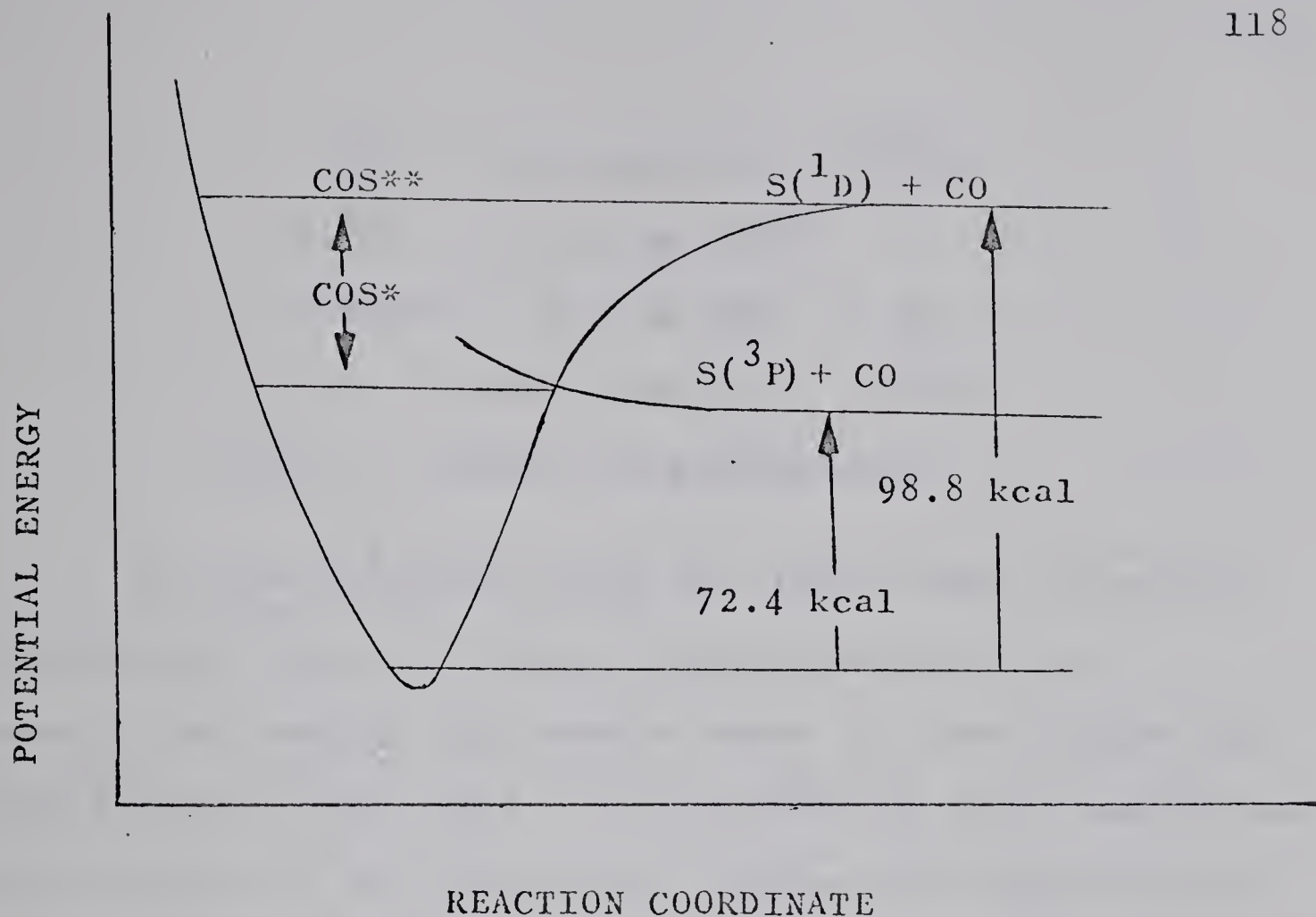
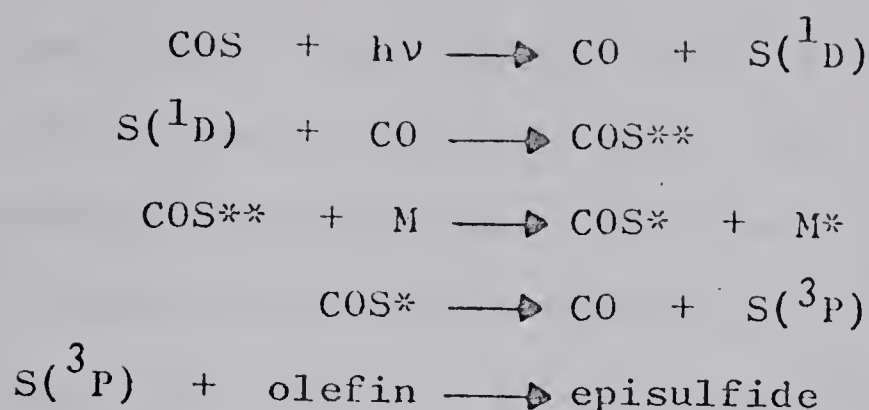


Fig. 14. Schematic diagram of COS potential curves.

In the diagram, COS\* represents an excited COS which may have undergone partial vibrational deactivation by other molecules, but still lies in the energy region where the dissociation to CO + S(<sup>3</sup>P) is energetically possible. While predissociation may occur at a number of stages in the over-all process of vibrational deactivation, the rate of deactivation of the association complex to energy levels below that required for predissociation must be small. This is shown by the rate of sulfur product formation in Table XXXIII, which does not decrease with increasing partial pressures of CO. For this system, the mechanism would be as follows:





For the  $\text{O}(^1\text{D})$ -CO system in liquid Argon, when the oxygen atom source is ozone, predissociation of the association complex  $\text{CO}_2^*$  occurs about 15 times faster than deactivation to  $\text{CO}_2$  (90). In the  $\text{S}(^1\text{D})$ -CO inert gas system, deactivation of the association complex  $\text{COS}^*$  appears to be absent. This indicates that in the gas phase, predissociation of the complex must be rapid compared to vibrational energy transfer.

Reactions of recoil  $^{35}\text{S}$ -atoms with CO, however, resulted in the formation of  $\text{CO}^{35}\text{S}$  (91). The  $^{35}\text{S}$  atoms were produced by the nuclear reaction  $^{35}\text{Cl}(\text{n},\text{p})^{35}\text{S}$ , and in gaseous CO- $\text{C}_2\text{F}_4\text{Cl}_2$  mixtures, 85% of the  $^{35}\text{S}$  atoms were scavenged by CO to yield  $\text{CO}^{35}\text{S}$ . This may indicate that the  $\text{C}_2\text{F}_4\text{Cl}_2$  molecule, which was inert to attack by  $^{35}\text{S}$  atoms, is very efficient in deactivating the association complex to levels below that required for dissociation.

## 2) The effect of wavelength of exciting radiation

A marked change in product distribution was observed for the COS- $\text{C}_2\text{H}_4$  system when the wavelength of the photolytic





light was decreased. The data of Table XI (Chapter IV), which is illustrated in Fig. 15, show that larger yields of vinyl mercaptan were obtained with the Cd ( $2288 \text{ \AA}^{\circ}$ ) and Zn ( $2139 \text{ \AA}^{\circ}$ ) lamps than with the Hg-arc ( $2490 \text{ \AA}^{\circ}$ ) when corrections are made for secondary photodecomposition. A similar effect was noted for the propylene and 1,1-difluoroethylene systems (Table XX, Chapter IV).

The wavelengths of photolysis for the Hg-arc, Cd and Zn lamps correspond to energies of 114, 124 and 134 kcal./mole respectively. Since the formation of  $S(^1D)$  atoms from COS requires ca. 99 kcal./mole, the average excess energy will be 15, 25 and 35 kcal./mole for photolysis at 2490, 2288 and  $2139 \text{ \AA}^{\circ}$  respectively.

Although the exact partitioning of this excess energy between the S-atom and CO is not known, it is reasonable that the translational energy of S-atoms will be greater for higher energy photolysis. The increased  $R(VM)/R(ES)$  ratio at the shorter wavelengths may then be attributed to increased translational energy of the S-atoms. Experimental verification, that the effect is due to translationally energized  $S(^1D)$  atoms, was obtained by adding Xenon to the  $C_2H_4$  system. The data in Table XXXIV shows that at higher partial pressures of Xenon, the ratio  $R(VM)/R(ES)$  is decreased to ca. 1 for  $2288 \text{ \AA}^{\circ}$  photolysis. Xenon, which was shown to be inefficient for electronic relaxation of singlet sulfur atoms, is expected





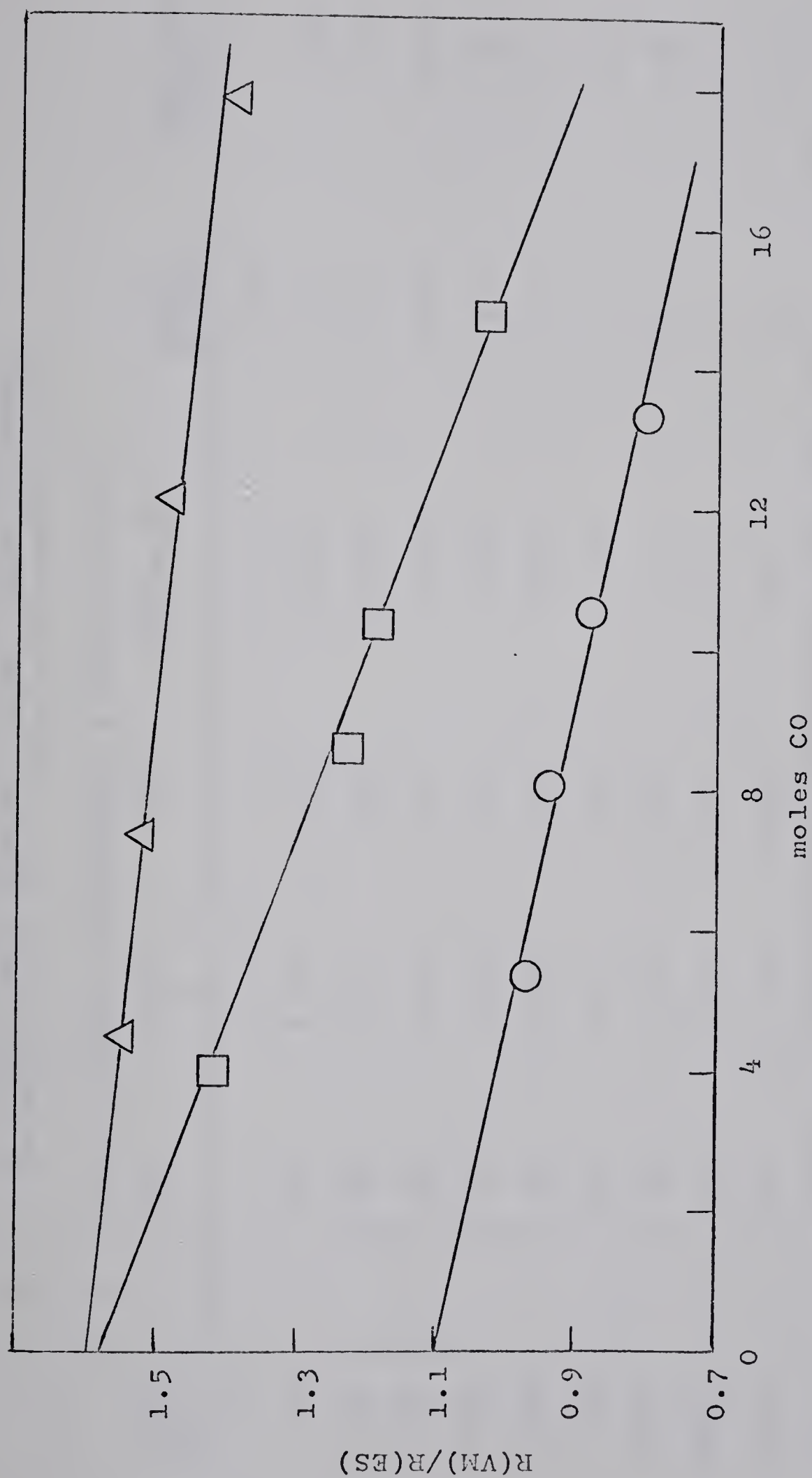


Fig. 15 Relative rates for vinyl mercaptan and ethylene episulfide formation as a function of CO yield in the  $\text{COS-C}_2\text{H}_4$  system.  $\triangle$  = Cd lamp photolysis;  $\square$  = Zn lamp photolysis;  $\circ$  = med. pressure Hg arc photolysis



TABLE XXXIV

## RATES OF PRODUCT FORMATION AS A FUNCTION

OF ADDED XENON PRESSURE IN THE COS-C<sub>2</sub>H<sub>4</sub> SYSTEM<sup>a</sup>

P(Xe), torr	Rates, $\mu\text{moles/min.} \times 10$					$\frac{\Sigma R(\text{VM, ES})}{R(\text{CO})}$	$\frac{R(\text{VM})}{R(\text{ES})}$	$\frac{\Sigma R(\text{VM, ES})}{R(\text{CO})}$
	CO	VM <sup>b</sup>	ES <sup>b</sup>	$\Sigma R(\text{VM, ES})$				
0	..	..	..	..	..	1.36	..	..
50	0.96	0.38	0.29	0.67	0.67	1.31	0.70	0.70
100	0.94	0.37	0.28	0.65	0.65	1.32	0.69	0.69
200	0.91	0.36	0.28	0.64	0.64	1.28	0.70	0.70
300	0.93	0.35	0.29	0.64	0.64	1.21	0.69	0.69
400	0.91	0.35	0.29	0.64	0.64	1.21	0.70	0.70
600	0.91	0.35	0.30	0.65	0.65	1.17	0.71	0.71
800	0.93	0.35	0.31	0.66	0.66	1.13	0.71	0.71
1000	0.91	0.34	0.32	0.66	0.66	1.07	0.72	0.72
1200	0.91	0.34	0.33	0.67	0.67	1.03	0.73	0.73

<sup>a</sup>P(COS) = 100 torr; P(C<sub>2</sub>H<sub>4</sub>) = 400 torr; exposure time = 30 min.; light source, Cd spectral lamp

<sup>b</sup>VM = vinyl mercaptan; ES = ethylene episulfide



to be a good energy sink for excess translational energy. Thus, from a comparison of the magnitude of change in  $R(\text{VM})/R(\text{ES})$  with added Xenon for photolysis by the Hg-arc and Cd lamps, it is apparent that the effect is due to the excess kinetic energy of  $\text{S}(^1\text{D})$  atoms.

An increase in the rate of insertion with increasing energy of photolytic light was also attributed to excess translational energy of  $\text{S}(^1\text{D})$  atoms for the reactions of sulfur atoms with paraffins (65).

### 3) The effect of temperature

The rate of CO formation increases rapidly with temperature in the Hg-arc photolysis of pure COS as shown in Table XXXV. Since the primary quantum yield for CO formation from COS is at least 0.91 (66), the temperature dependence of CO formation may arise from the positive temperature coefficient of the COS absorption at the long-wavelength end of the spectrum. From a least mean square calculation of the Arrhenius equation, an apparent activation energy of  $2.7^{+0.1}$  kcal./mole was obtained for the absorption coefficient of COS for Hg-arc ( $2490 \text{ \AA}$ ) photolysis. The fundamental frequencies of the C-S stretching and bending modes of the linear COS molecule are  $859 \text{ cm}^{-1}$  (2.5 kcal./mole) and  $527 \text{ cm}^{-1}$  (1.5 kcal./mole) respectively (92)





TABLE XXXV

RATE OF CO FORMATION IN THE Hg-ARC PHOTOLYSIS OF COS  
AS A FUNCTION OF TEMPERATURE<sup>a</sup>

$\frac{1}{T, ^\circ\text{K}} \times 10^3$	R(CO), $\mu\text{moles}$	R(CO) <sup>b</sup>
2.52	5.54	1.00
2.38	6.43	1.16
2.25	7.32	1.32
2.08	10.02	1.81
2.00	11.17	2.02
1.92	11.95	2.16

<sup>a</sup>P(COS) = 100 torr; exposure time = 15 min.;

light source, med. pressure Hg arc

<sup>b</sup>relative to R(CO) as unity at 124°C



and the temperature effect may indicate a non-linear upper state.

The effect of temperature on the olefin-COS systems is shown in Tables XXXVI - XXXVIII for Hg-arc photolysis. For the ethylene, propylene and 1,1-difluoroethylene systems, the only observable change occurred in the  $R(\text{mercaptan})/R(\text{episulfide})$  ratio, which showed an increase with elevation of temperatures. The temperature range was limited by the thermal stability of products; vinyl mercaptan underwent a slow decomposition at  $150^{\circ}\text{C}$ , while the other products were stable up to ca.  $200^{\circ}\text{C}$ . From least mean square calculations of the Arrhenius equation, activation energy differences and relative A values for mercaptan and episulfide formation were obtained for these systems. These are summarized in Table XXXIX.

Although these activation energy differences are small, they appear to be real. The values are not directly comparable since activation energies of addition processes probably vary with olefin structure (Chapter VI). However, from the data on the propylene system, the activation energy of the methyl insertion reaction has the same order of magnitude as that of propene-1-thiol forming step. While this result is compatible with direct insertion for the formation of both types of mercaptans, it does not necessarily exclude the formation of the vinylic mercaptan by some other mechanism.



TABLE XXXVI

## RATES OF PRODUCT FORMATION IN THE Hg-ARC PHOTOLYSIS OF COS

WITH ADDED ETHYLENE AS A FUNCTION OF TEMPERATURE<sup>a</sup>

Temp °C	Rates, $\mu\text{moles/min.} \times 10$					$\frac{R(\text{VM})}{R(\text{ES})}$	$\frac{\Sigma R(\text{VM, ES})}{R(\text{CO})}$
	CO	VM	ES	$\Sigma R(\text{VM, ES})$			
28	2.46	0.80	0.80	1.60	1.00	0.65	
59	3.12	1.10	0.96	2.06	1.15	0.66	
80	3.20	1.17	0.96	2.13	1.22	0.66	
105	3.70	1.33	1.09	2.42	1.22	0.65	
126	4.03	1.53	1.21	2.74	1.27	0.65	
150	4.55	1.83	1.37	3.20	1.34	0.70	
175	5.30	1.98	1.53	3.51	1.30	0.66	
198	5.96	2.15	1.69	3.84	1.27	0.64	
226	7.10	2.42	1.94	4.36	1.26	0.61	
251	7.70	2.30	2.13	4.43	1.06	0.58	

<sup>a</sup>P(COS) = 100 torr; P(C<sub>2</sub>H<sub>4</sub>) = 300 torr; exposure time = 15 min.



TABLE XXXVII

## RATES OF PRODUCT FORMATION IN THE 2537 Å PHOTOLYSIS OF COS

WITH ADDED PROPYLENE AS A FUNCTION OF TEMPERATURE<sup>a</sup>

$\frac{1}{T, ^\circ K} \times 10^3$	Rates, $\mu\text{moles/min.} \times 10^{-4}$					$\frac{R(\text{AM})}{R(\text{PS})}$	$\frac{R(\text{MVM})}{R(\text{PS})}$	$\frac{\Sigma R(\text{AM, MVM, PS})}{R(\text{CO})}$
	CO	AM	MVM	PS				
3.37	2.70	0.30	0.32	1.22		0.25	0.26	0.69
3.12	3.17	0.38	0.42	1.41		0.27	0.30	0.70
2.86	3.67	0.47	0.53	1.54		0.30	0.35	0.69
2.68	4.73	0.62	0.69	1.77		0.35	0.39	0.65
2.53	5.42	0.74	0.85	2.23		0.33	0.38	0.70
2.36	5.83	0.79	0.91	2.26		0.35	0.40	0.68
2.22	6.62	0.91	1.07	2.55		0.36	0.42	0.67
2.09	6.60	0.91	1.11	2.53		0.36	0.44	0.69
2.01	7.69	1.04	1.23	2.72		0.38	0.45	0.65
1.89	8.04	1.14	1.47	2.94		0.39	0.50	0.69

<sup>a</sup>P(COS) = 100 torr; P(C<sub>3</sub>H<sub>6</sub>) = 400 torr; light source, high intensity

Hg resonance lamp





TABLE XXXVIII

RATES OF PRODUCT FORMATION IN THE Hg-ARC PHOTOLYSIS OF COS  
WITH ADDED 1,1-DIFLUOROETHYLENE AS A FUNCTION OF TEMPERATURE<sup>a</sup>

$\frac{1}{T, ^\circ K} \times 10^3$	Rates, $\mu\text{moles/min.} \times 10^3$				
	CO	DFVM	DFES	$\frac{R(\text{DFVM})}{R(\text{DFES})}$	$\frac{\Sigma R(\text{DFVM}, \text{DFES})}{R(\text{CO})}$
3.37	1.96	0.40	0.86	0.46	0.64
3.06	2.42	0.49	1.04	0.47	0.63
2.86	2.89	0.62	1.25	0.49	0.65
2.69	3.31	0.77	1.41	0.54	0.66
2.49	3.91	0.90	1.60	0.56	0.64
2.36	4.25	1.02	1.75	0.58	0.65
2.19	5.44	1.35	2.19	0.61	0.65
2.10	5.93	1.43	2.29	0.62	0.63
1.99	6.44	1.55	2.54	0.61	0.64
1.90	7.18	1.88	2.94	0.64	0.67

<sup>a</sup>P(COS) = 100 torr; P(CF<sub>2</sub>CH<sub>2</sub>) = 400 torr; light source,  
med. pressure Hg-arc



TABLE XXXIX

RELATIVE A VALUES AND ACTIVATION ENERGY DIFFERENCES  
 FOR THE FORMATION OF MERCAPTANS AND EPISULFIDES IN THE REACTION  
 OF S ATOMS WITH ETHYLENE, PROPYLENE AND 1,1-DIFLUOROETHYLENE<sup>a</sup>

$$E_a(\text{VM}) - E_a(\text{ES}) = 0.55^{+0.08} \text{ kcal/mole}$$

$$E_a(\text{AM}) - E_a(\text{PS}) = 0.58^{+0.07} \text{ kcal/mole}$$

$$E_a(\text{MVM}) - E_a(\text{PS}) = 0.77^{+0.07} \text{ kcal/mole}$$

$$E_a(\text{DFVM}) - E_a(\text{DFES}) = 0.48^{+0.04} \text{ kcal/mole}$$

$$\frac{A(\text{VM})}{A(\text{ES})} = 2.5^{+0.2}$$

$$\frac{A(\text{MVM})}{A(\text{PS})} = 1.1^{+0.1}$$

$$\frac{A(\text{AM})}{A(\text{PS})} = 0.70^{+0.07}$$

$$\frac{A(\text{DFVM})}{A(\text{DFES})} = 1.2^{+0.2}$$

---

<sup>a</sup>From least mean square calculations, with errors quoted as the  
 standard deviation



Since the activation energies of mercaptan formation are 0.4 - 0.8 kcal./mole larger than those of episulfide formation, the increase in relative yields of the former at shorter wavelengths is due to excess translational energy of  $S(^1D)$  atoms. The difference in reactivity should then gradually diminish as the temperature is raised, since the activation energy differences are small. Thus in the 2288 Å photolysis of ethylene- and propylene-COS systems, a change in temperature to ca. 200°C causes no apparent alteration in the reaction as shown in Tables XL and XLI. Furthermore, from comparison of the data for 2490 Å and 2288 Å photolysis of the ethylene system, it may be concluded that the average difference in excess translational energy of  $S(^1D)$  atoms from the two photolytic light sources is not larger than 3 kcal./mole at the instant of reaction. This is based on the fact that at about 225°C the ratio  $R(VM)/R(ES)$  for the Hg-arc photolysis will be the same as for photolysis by the Cd lamp at room temperature, and the total excess translational energy in the S-atom and  $C_2H_4$  molecule will be ca. 3 kcal./mole larger at 225°C.

#### 4) The effect of deuteration

To determine whether C-H extension is important in definition of the reaction coordinate for  $S(^1D)$ -olefin reactions, the reaction was carried out with ethylene- $d_4$ . The results in Table XLII show that no change, within





TABLE XL

## RATES OF PRODUCT FORMATION IN THE 2288 Å PHOTOLYSIS OF COS

WITH ADDED ETHYLENE AS A FUNCTION OF TEMPERATURE<sup>a</sup>

Temp °C	Rates, $\mu\text{moles/min.} \times 10$				$\frac{R(\text{VM})}{R(\text{ES})}$	% recovery
	CO	VM	ES	$\Sigma R(\text{VM}, \text{ES})$		
26	0.85	0.37	0.26	0.63	1.42	97
52	0.84	0.37	0.25	0.61	1.47	95
77	0.84	0.38	0.26	0.64	1.46	100
102	0.86	0.37	0.24	0.61	1.53	95
128	0.87	0.35	0.26	0.61	1.35	95
154	0.87	0.35	0.25	0.60	1.40	94
179	0.84	0.32	0.22	0.54	1.45	84

<sup>a</sup> $P(\text{COS}) = 100$  torr;  $P(\text{C}_2\text{H}_4) = 411$  torr; exposure time = 30 min.;  $R^\circ(\text{CO}) = 1.48$   
 ( $\mu\text{moles/min.} \times 10$ )

<sup>b</sup>% recovery of condensables in terms of  $R^\circ(\text{CO}) - R(\text{CO})$



TABLE XLI

## RATES OF PRODUCT FORMATION IN THE 2288 Å PHOTOLYSIS OF COS

WITH ADDED PROPYLENE AS A FUNCTION OF TEMPERATURE<sup>a</sup>

Temp °C	Rates, $\mu\text{moles/min.} \times 10$					$\frac{\Sigma R(\text{MVM, AM})}{R(\text{PS})}$
	CO	MVM	AM	PS	$\Sigma R(\text{MVM, AM, PS})$	
50	0.91	0.15	0.16	0.38	0.69	0.82
79	0.89	0.16	0.16	0.38	0.70	0.84
105	0.91	0.16	0.16	0.38	0.70	0.84
127	0.91	0.17	0.15	0.38	0.70	0.84
149	0.99	0.18	0.16	0.40	0.74	0.85
176	0.96	0.17	0.16	0.39	0.72	0.85
202	0.94	0.18	0.17	0.38	0.73	0.92
224	0.97	0.18	0.16	0.38	0.72	0.89

<sup>a</sup>P(COS) = 100 torr; P(C<sub>3</sub>H<sub>6</sub>) = 410 torr; exposure time = 30 min.



TABLE XLII

RATES OF PRODUCT FORMATION IN THE COS-C<sub>2</sub>D<sub>4</sub> SYSTEM

Light Source	Rates, $\mu\text{moles/min.} \times 10$				$\frac{R(\text{VM})}{R(\text{ES})}$	$\frac{R(\text{VM})/R(\text{ES})}{\frac{D}{H}} = \frac{C}{H}$
	CO	VM	ES			
Med. pressure Hg-arc <sup>a</sup>	3.77	1.02	1.14	0.89		0.90
	4.05	1.23	1.37	0.90		0.94
Cd spectral lamp <sup>b</sup>	0.80	0.33	0.25	1.3		1.3
	0.79	0.33	0.25	1.3		1.4

<sup>a</sup>P(COS) = 100 torr; P(C<sub>2</sub>D<sub>4</sub>) = 400 torr; exposure time = 15 min.<sup>b</sup>P(COS) = 100 torr; P(C<sub>2</sub>D<sub>4</sub>) = 407 torr; exposure time = 30 min.<sup>c</sup>from Table V<sup>d</sup>from Table XL



experimental error, was observed in the  $R(\text{VM})/R(\text{ES})$  ratio upon deuteration. This suggests that no significant C-H bond stretching occurs in the transition state. Thus the lack of an isotope effect provides no information for distinguishing between isomerization of the episulfide or insertion as the mode of formation of vinylic mercaptans, since the result may be consistent with either mechanism. No deuterium isotope effect was observed in the paraffin- $\text{S}(^1\text{D})$  atom system as well (65).

Deuterium isotope effects of the order  $k_{\text{H}}/k_{\text{D}} = 1.5 - 2.0$  have been observed for methylene insertion into allylic and vinylic C-H bonds of cis-2-butene (93). A secondary isotope effect for double bond addition was small. Apparently C-H extension is important in the activated complex for larger attacking species such as methylene.



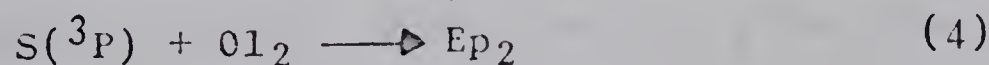
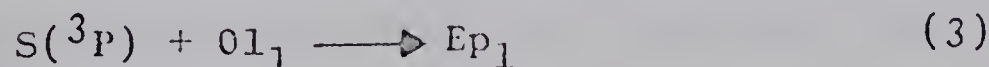
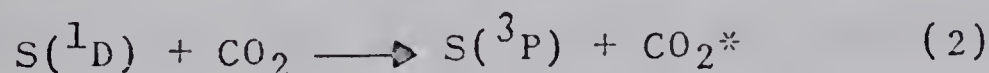


## CHAPTER VI

### THE RELATIVE RATES OF ADDITION OF SULFUR ATOMS TO FLUORINATED OLEFINS

Recent measurements of the relative rates of addition of triplet sulfur atoms to a representative set of olefins indicate that the ground-state atoms display considerable electrophilic character (70). A linear correlation between the rate of addition and ionization potential of the parent olefin was found, suggesting that a polar transition state, such as an outer charge-transfer or  $\pi$ -complex, is involved. In order to determine the effect of electronegative substituents on the reactivity of  $S(^3P)$  atoms towards olefins, three fluorinated olefin systems were investigated.

The relative reactivities of vinyl fluoride, 1,1-difluoroethylene and trifluoroethylene were obtained by observing the  $S(^3P)$  reaction with a fixed mixture of each olefin and ethylene as a function of temperature.  $S(^3P)$  atoms were obtained by the collisional deactivation of singlet sulfur atoms, through the use of a large excess of  $CO_2$ . The reaction scheme for these systems will be:





where  $Ol_1$  represents the fluorinated ethylene,  $Ol_2$  represents ethylene and  $Ep_1$  and  $Ep_2$  the corresponding episulfides. The relative reactivities are then given by the expression

$$\frac{k_3}{k_4} = \frac{R(Ep_1)}{R(Ep_2)} \frac{Ol_2}{Ol_1}$$

In a previous investigation (70), small positive intercepts were observed for the rates of ethylene episulfide and propylene episulfide formation as a function of CO yield in the  $C_2H_4-C_3H_6-S(^3P)$  atom system and were attributed to secondary photodecomposition. Since the results in Table XLIII and Fig. 16 verify this, conversion in the present study was kept down to about 1%.

The results obtained for the fluorinated olefin systems are shown in Tables XLIV - XLVI. The episulfides are thermally stable to ca. 200°C, except for trifluoroethylene episulfide which began to undergo a slow decomposition at 150°C. Hence calculations for activation energy differences and relative A values for this system were completed using only those values up to 150°C. The relative rates, activation energy differences and relative A values, all compared to ethylene, are summarized in Table XLVII.

A comparison of the halogenated and hydrocarbon olefins in Table XLVIII and Fig. 17 shows that the correlation between ionization potential and relative reactivity only holds for the hydrocarbon series. Quantitatively, the electron density



TABLE XLIII

ADDITION OF  $S(^3P)$  ATOMS TO ETHYLENE AND PROPYLENE<sup>a</sup>  
 RELATIVE RATES AS A FUNCTION OF CO YIELD FOR  $[C_2H_4]/[C_3H_6] = 4.18$

Yields, $\mu\text{moles}$		PS	$k[S(^3P) + C_3H_6]^b$	$\frac{\Sigma R(ES, PS)}{R(CO)}$
CO	ES			
1.04	0.298	0.473	6.66	0.74
1.56	0.433	0.710	6.85	0.73
2.25	0.602	0.980	6.80	0.71
3.08	0.799	1.32	6.90	0.69

<sup>a</sup> $P(COS) = 21.3$  torr;  $P(CO_2) = 1114$  torr;  $P(C_2H_4) = 52.6$  torr;

$P(C_3H_6) = 12.6$  torr; light source, med. pressure Hg-arc

<sup>b</sup>corrected for pressure,  $k \frac{[S(^3P) + C_3H_6]}{[S(^3P) + C_2H_4]} = \frac{R(PS)}{R(ES)} \times \frac{P(C_2H_4)}{P(C_3H_6)}$





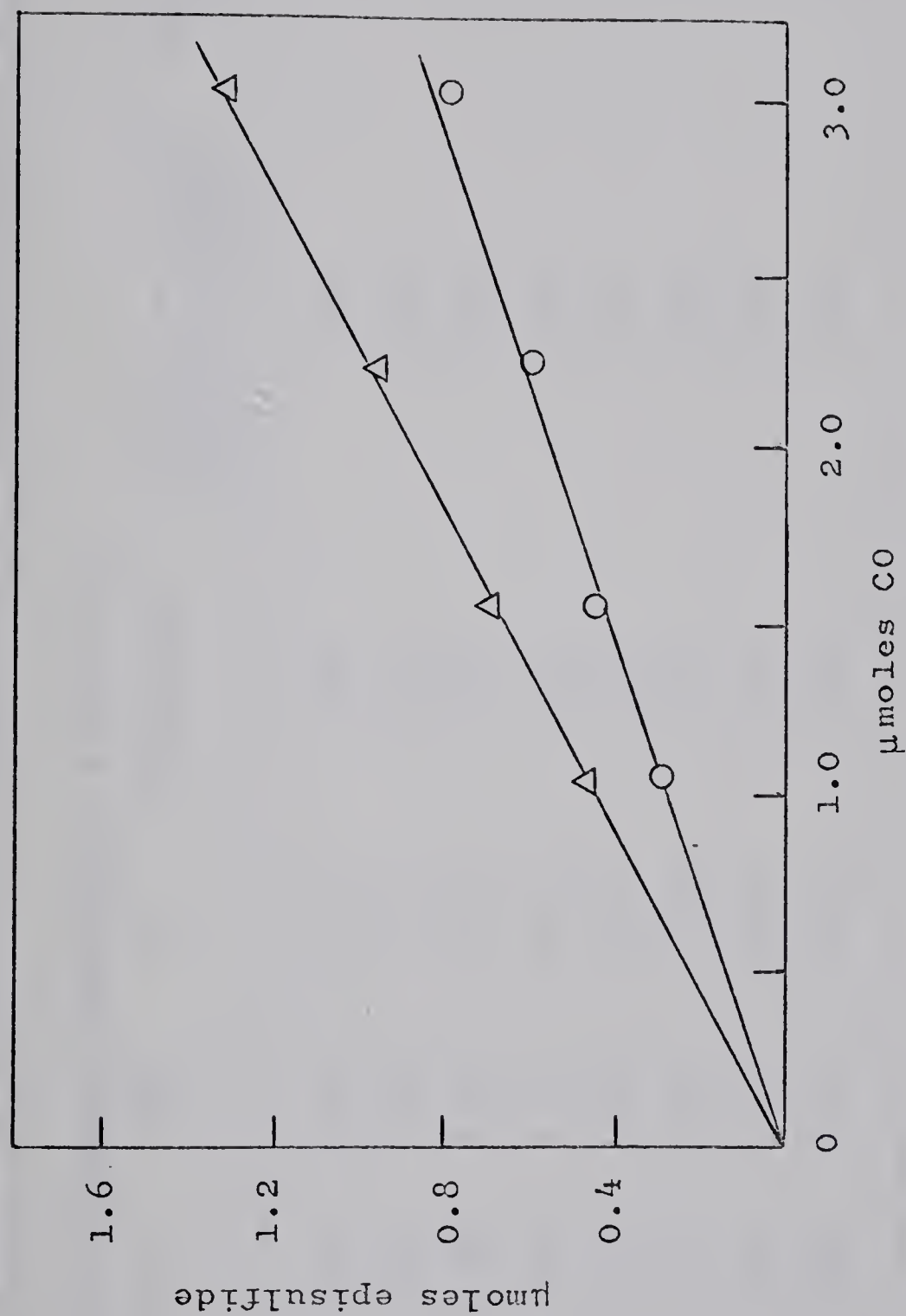


Fig. 16 Addition of  $S(^3P)$  atoms to ethylene and propylene. Episulfide vs. CO yields for  $(C_2H_4)/(C_3H_6) = 4.18$ . O = ethylene episulfide;  $\Delta$  = propylene episulfide



TABLE XLIV

ADDITION OF S(<sup>3</sup>P) ATOMS TO ETHYLENE AND VINYL FLUORIDE<sup>a</sup>RELATIVE RATES AS A FUNCTION OF TEMPERATURE FOR  $[C_2H_4]/[C_2H_3F] = 0.924$ 

$\frac{1}{T^0} \times 10^3$	Rates, $\mu\text{moles/min.} \times 10$				$\frac{k[S(^3P) + C_2H_3F]^b}{k[S(^3P) + C_2H_4]}$	$\frac{\Sigma R(FES, ES)}{R(CO)}$
	CO	FES	ES	$\Sigma R(FES, ES)$		
3.36	2.16	0.21	0.77	0.98	0.42	0.45
3.36	1.98	0.20	0.73	0.93	0.43	0.47
2.96	2.26	0.30	0.92	1.22	0.51	0.54
2.62	2.46	0.37	0.99	1.36	0.57	0.55
2.51	2.74	0.39	1.07	1.46	0.57	0.55
2.38	2.74	0.41	1.08	1.49	0.59	0.55
2.20	2.24	0.37	0.86	1.23	0.66	0.55
2.10	2.50	0.41	0.95	1.36	0.67	0.54

<sup>a</sup> $P(COS) = 12.4$  torr;  $P(CO_2) = 1207$  torr;  $P(C_2H_4) = 30.3$  torr;  $P(C_2H_3F) = 32.8$  torr;  
light source, Cd spectral lamp; exposure time = 10 min.

<sup>b</sup>corrected for pressure and yield of FES,  $\frac{k[S(^3P) + C_2H_3F]}{k[S(^3P) + C_2H_4]} = \frac{R(FES)}{R(ES)} \times \frac{P(C_2H_4)}{P(C_2H_3F)} \times \frac{100}{60}$



TABLE XLV

ADDITION OF S(<sup>3</sup>P) ATOMS TO ETHYLENE AND 1,1-DIFLUOROETHYLENE<sup>a</sup>RELATIVE RATES AS A FUNCTION OF TEMPERATURE FOR  $[C_2H_4]/[C_2F_2H_2] = 0.468$ 

$\frac{1}{T} \times 10^3$ °K	Rates, $\mu\text{moles/min.} \times 10$					$\frac{\Sigma R(\text{DFES, ES})}{R(\text{CO})}$
	CO	DFES	ES	$\Sigma R(\text{DFES, ES})$	$\frac{k[S(^3P) + C_2F_2H_2]^b}{k[S(^3P) + C_2H_4]}$	
3.36	2.23	0.10	0.79	0.89	0.10	0.40
3.02	2.07	0.15	0.80	0.95	0.15	0.46
2.86	2.17	0.20	0.88	1.08	0.17	0.50
2.69	2.33	0.21	0.89	1.10	0.18	0.47
2.50	2.40	0.25	0.92	1.17	0.22	0.49
2.35	2.44	0.28	0.90	1.18	0.24	0.48
2.22	2.57	0.37	0.94	1.21	0.30	0.47

<sup>a</sup> $P(\text{COS}) = 11.6$  torr;  $P(\text{CO}_2) = 1209$  torr;  $P(\text{C}_2\text{H}_4) = 21.5$  torr;  $P(\text{C}_2\text{F}_2\text{H}_2) = 46.0$  torr;  
light source, Cd spectral lamp; exposure time = 10 min.

<sup>b</sup>corrected for pressure and yield of DFES,  $\frac{k[S(^3P) + C_2F_2H_2]}{k[S(^3P) + C_2H_4]} = \frac{R(\text{DFES})}{R(\text{ES})} \times \frac{P(\text{C}_2\text{H}_4)}{P(\text{C}_2\text{F}_2\text{H}_2)} \times \frac{100}{60}$



TABLE XLVI

ADDITION OF S(<sup>3</sup>P) ATOMS TO ETHYLENE AND TRIFLUOROETHYLENE<sup>a</sup>RELATIVE RATES AS A FUNCTION OF TEMPERATURE FOR  $[C_2H_4]/[C_2F_3H] = 0.353$ 

$\frac{1}{T^{\circ}K} \times 10^3$	Rates, $\mu\text{moles/min.} \times 10$					$\frac{\Sigma R(TFES, ES)}{R(CO)}$
	CO	TFES	ES	$\Sigma R(TFES, ES)$	$\frac{k[S(^3P) + C_2F_3H]^b}{k[S(^3P) + C_2H_4]}$	
3.36	2.07	0.057	0.56	0.62	0.072	0.30
3.09	2.34	0.14	0.99	1.13	0.096	0.48
2.90	2.41	0.17	1.03	1.20	0.12	0.50
2.68	2.26	0.19	0.96	1.15	0.14	0.51
2.51	1.93	0.17	0.80	0.97	0.15	0.50
2.35	2.08	0.10	0.83	0.93	0.087	0.45
2.15	2.89	0.09	0.84	0.93	0.077	0.32

<sup>a</sup> $P(COS) = 13.9$  torr;  $P(CO_2) = 1266$  torr;  $P(C_2H_4) = 21.6$  torr;  $P(C_2F_3H) = 61.2$  torr; light source, Cd spectral lamp; exposure time = 10 min.

<sup>b</sup>corrected for pressure and yield of TFES,  $\frac{k[S(^3P) + C_2F_3H]}{k[S(^3P) + C_2H_4]} = \frac{R(TFES)}{R(ES)} \times \frac{P(C_2H_4)}{P(C_2F_3H)} \times \frac{100}{50}$





TABLE XLVII

RELATIVE RATES, ACTIVATION ENERGY DIFFERENCES AND RELATIVE A VALUES FOR THE  
ADDITION OF S(<sup>3</sup>P) ATOMS TO C<sub>2</sub>H<sub>4</sub> AND C<sub>2</sub>FH<sub>3</sub>, C<sub>2</sub>H<sub>4</sub> AND 1,1-CF<sub>2</sub>CH<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> AND C<sub>2</sub>F<sub>3</sub>H

Olefin	$\frac{k[S(^3P) + \text{olefin}]^a}{k[S(^3P) + C_2H_4]}$	$E_a(\text{olefin}) - E_a(C_2H_4)^b$ kcal./mole	$\frac{A(\text{olefin})^b}{A(C_2H_4)}$
C <sub>2</sub> FH <sub>3</sub>	0.42	$0.73 \pm 0.05$	$1.4 \pm 0.1$
1,1-CF <sub>2</sub> CH <sub>2</sub>	0.10	$1.7 \pm 0.2$	$1.9 \pm 0.3$
C <sub>2</sub> F <sub>3</sub> H	0.07	$2.0 \pm 0.2$	$2.1 \pm 0.5$

<sup>a</sup> at 25° centrigrade

<sup>b</sup> from least mean square calculations, with errors quoted as the standard deviation



TABLE XLVIII

RELATIVE REACTIVITY, RELATIVE A VALUES AND  
 ACTIVATION ENERGY DIFFERENCES FOR S(<sup>3</sup>P) ATOM  
 REACTIONS WITH OLEFINS

Olefin	k rel. <sup>a</sup>	A/A <sub>eth</sub> <sup>c</sup>	E <sub>eth</sub> -E <sup>c</sup>	I.P. (eV) <sup>d</sup>
ethylene	1.00	1.00	0	10.62
vinyl fluoride <sup>b</sup>	0.42	1.4	-0.73	10.37
1,1-difluoroethylene <sup>b</sup>	0.10	1.9	-1.7	10.30
trifluoroethylene <sup>b</sup>	0.07	2.1	-2.0	10.14
vinyl chloride	1.4	...	...	9.99
propylene	6.8	1.0	1.14	9.84
1-butene	10	...	...	9.76
1-pentene	10	0.9	1.69	9.67
cyclopentene	18	0.8	2.12	9.27
<u>trans</u> -2-butene	20	0.7	2.01	9.27
<u>cis</u> -2-butene	16	0.5	2.09	9.34
isobutylene	50	1.0	2.30	9.26
2-methyl-1-butene	56	0.9	2.79	9.20

<sup>a</sup>k rel. = k(S + olefin)/k(S + C<sub>2</sub>H<sub>4</sub>), reference 70

<sup>b</sup>this work

<sup>c</sup>from reference 108

<sup>d</sup>from references 94 and 111



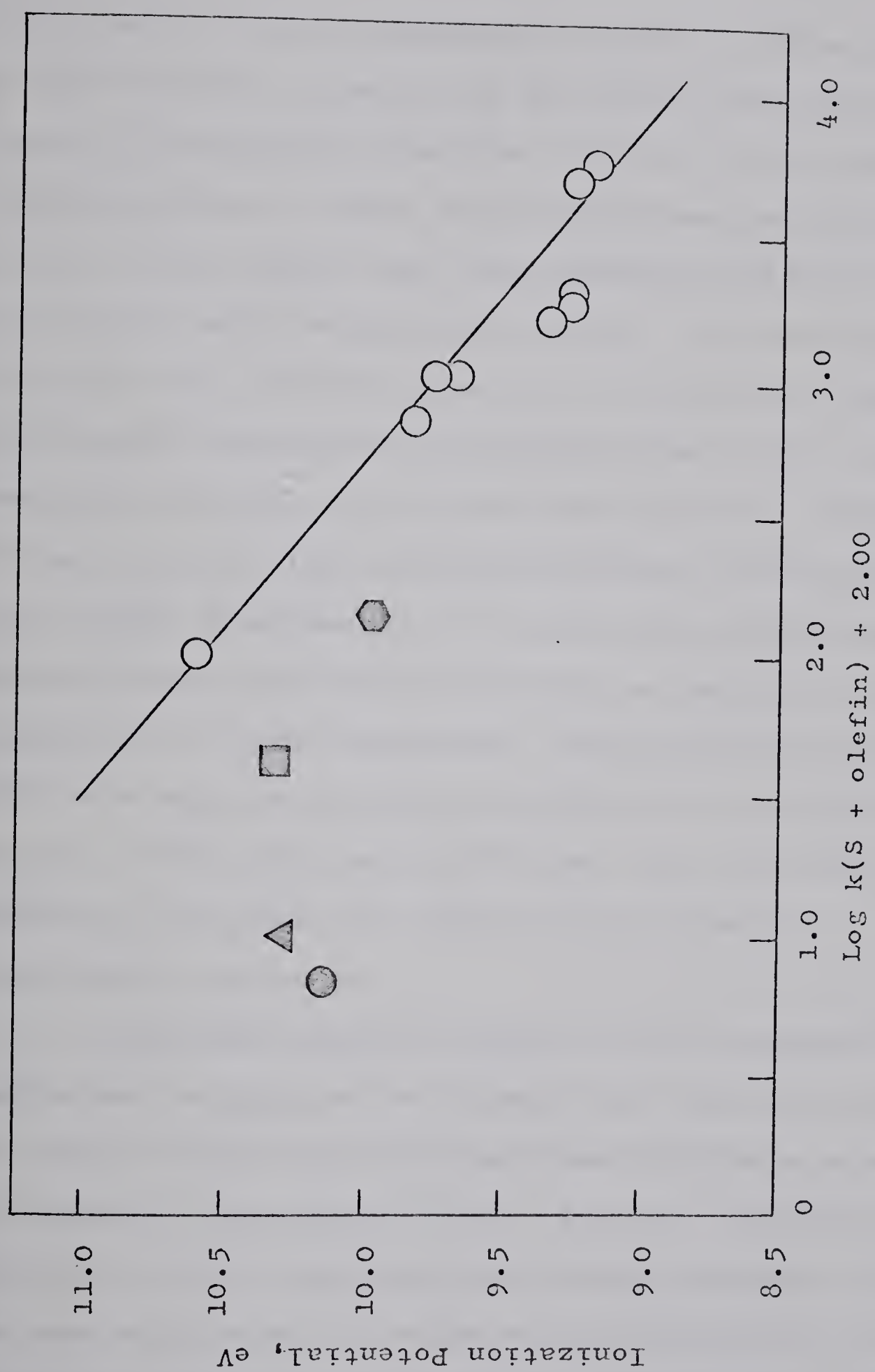


Fig. 17 Ionization Potentials vs.  $\log k$  for  $S(^3P)$  atom addition to olefins.

□ = vinyl fluoride; △ = 1,1-difluoroethylene; ○ = trifluoroethylene;  
 ● = vinyl chloride





of the double bond of hydrocarbon olefins is directly related to the ionization potential of the olefin and refers to the removal of an electron from the  $\pi$ -orbital. The electron-releasing effect of alkyl groups increases the electron density of the double bond, thus lowering the ionization potential of alkyl substituted olefins. The order of reactivity for the hydrocarbon set of olefins can then be explained by the increase of electron density in the double bond with increasing alkyl group substitution. Predictions of reactivity for the fluorinated olefins are in agreement, since highly electronegative fluorine atom substituents should decrease the electron density in the double bond, resulting in a lower reactivity. This indicates that the  $S(^3P)$  atom acts as an electron-seeking or electrophilic reagent.  $O(^3P)$  (49) and  $Se(^3P)$  atoms (61), two other members of the group six elements showed similar electrophilic character.

A decreased electron density in the  $\pi$ -system of the double bond is expected to increase the ionization potentials for vinyl chloride and the fluorinated ethylenes over that of ethylene. The smaller values, however, indicate that there is an effect opposing the induction process. This has been attributed to a resonance stabilization of the ionized resulting from structures such as  $C=C-F^+$  (94). The magnitude of the resonance effect increases with successive



substitution of fluorine atoms, as seen from the progressive reductions of the ionization potentials.

The deviation, from the inverse relationship between reactivity and ionization potential, by the fluorinated olefin systems could then be accounted for by the presence of resonance interactions in a charge-transfer type intermediate.

Linear correlations of reactivities with some physical property of the reacting olefin, such as that observed for the logarithms of the relative rate constants for  $S(^3P)$  addition to olefins with the ionization potentials of the olefins, have been used in attempts to formulate the structure of the transition-complex for addition reactions of electrophilic reagents and olefins. If a reaction series has a constant pre-exponential factor, the relationships may be expected to hold when the changes in activation energies caused by structural changes in the olefin are proportional to corresponding changes of some physical property of the homologous reactants. For addition reactions of electrophilic species and olefins it is usually considered that the pre-exponential factors in the Arrhenius rate equation are constant and as a result the logarithms of the reaction rate constants also correlate with physical properties of the olefins.

Sato and Cvetanovic (104) have shown that for electrophilic reagents such as  $O(^3P)$  atoms, peracetic acid,





$\text{Br}_2$  and  $\text{CBr}_2$ , the physical parameters of olefins that correlate with reactivity are properties of a double bond as a whole and not of the two individual carbon atoms in the double bond. Similar relationships were also found for  $\text{S}(^3\text{P})$  atom addition (105). Thus linear correlations of reactivity were found with parameters such as ionization potentials and excitation energies, but not with atom localization energies and free valences. The excitation energy represents the difference between the average energy of the excited triplet and singlet states and the ground state energy. Free valence is usually considered as a measure of the free radical character at a particular position in a molecule and atom localization energy represents the energy required to localize a  $\pi$ -electron on a carbon atom of the double bond.

Since these correlations indicate that the rate-determining step for addition of electrophilic species to olefins is an interaction with the double bond as a whole, Cvetanovic (57) tentatively suggests that the activated-complex can be represented as an outer charge-transfer or  $\pi$ -complex in contrast to a  $\sigma$ -complex where addition is associated with a carbon atom rather than a  $\text{C}=\text{C}$  bond. Although the double bond as a whole may be involved in the formation of the activated complex and determines the rate of addition, a three-membered ring intermediate or final product was not implied.

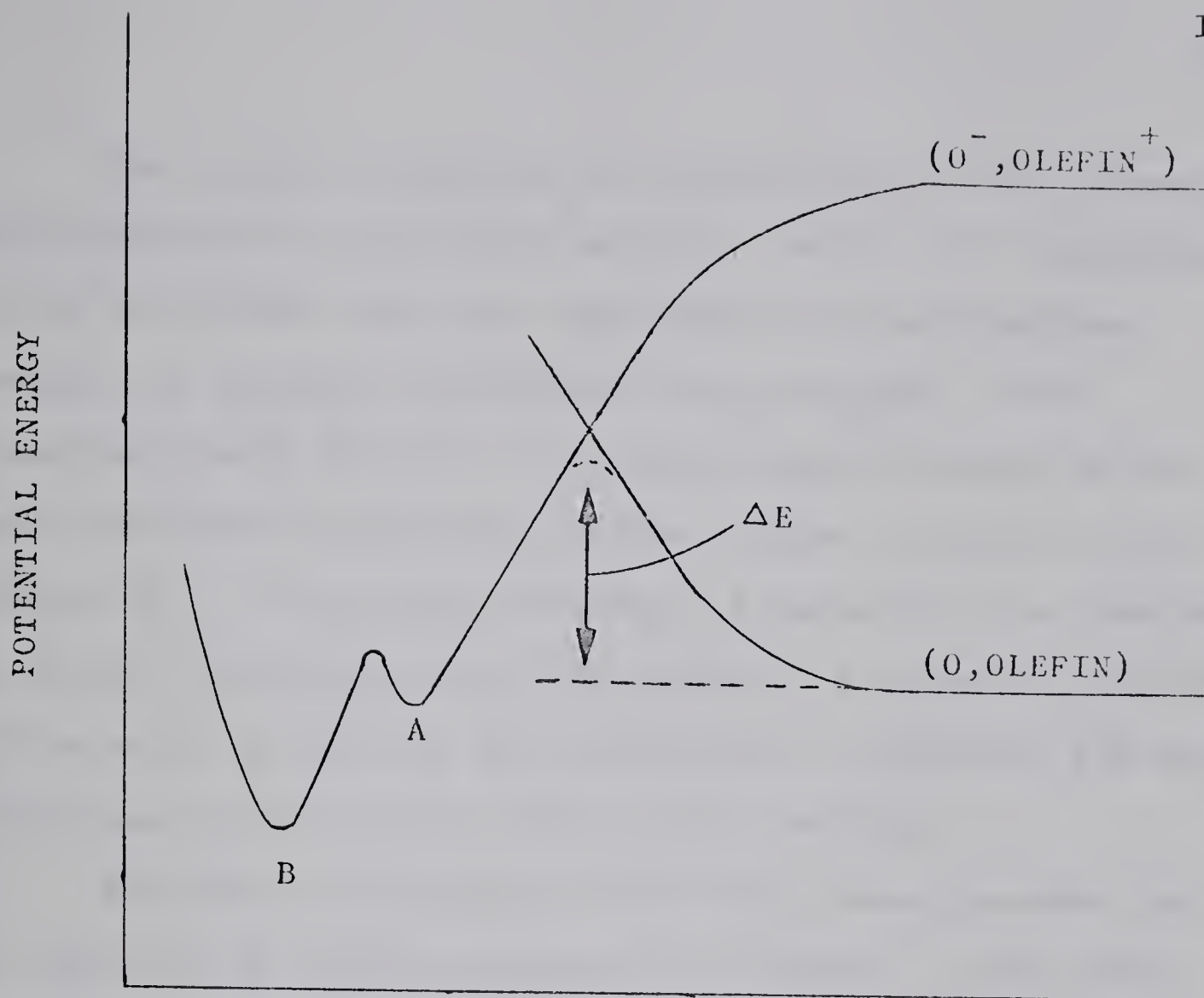


Cvetanovic (57) has shown that the differences in reactivities of  $O(^3P)$  atom addition to olefins are entirely due to differences in activation energies. The rates of addition of oxygen atoms to propylene and 1-butene were approximately the same as was found for 2-butene and 2-pentene. The effect of ethyl and methyl groups on reactivity are then about the same. From product composition it was found that orienting effects were also present. Oxygen atoms were found to add almost exclusively to the terminal carbon atom of the double bond in reactions with propylene and 1-butene. With 2-pentene the major addition took place at the carbon atom to which the methyl group is attached.

These results were taken as an indication that the initial interaction of oxygen atoms was with the double bond as a whole and that localization of the oxygen atom on one of the two carbon atoms of the original double bond takes place after the rate determining step, i.e. formation of the activated-complex. If the same factors governed reactivity and position of addition, approximately equal addition to the two doubly bonded carbon atoms in 2-pentene should have been observed. Fig. 17 illustrates the tentative schematic potential energy diagram that was proposed for the reaction.







REACTION COORDINATE

Fig. 17. Schematic potential energy-reaction coordinate diagram for the reaction of oxygen atoms with olefins.

As the  $O(^3P)$  atom approaches the olefinic double bond, the initial repulsion is opposed by an electrostatic interaction which leads to a lowering of the potential energy of the system. The electrostatic interaction may be brought about by partial charge transfer from the olefin to the attacking oxygen atom, i.e. polarization of the  $\pi$ -electrons in the intermediate complex. The minimum at A represents an outer charge-transfer or  $\pi$ -complex and that at B refers to the triplet biradical where the oxygen atom is localized on one of the two doubly-bonded atoms.



The initial repulsion is responsible for the potential energy barrier or activation energy. Hence, for a homologous series of olefins, the ease with which the intermediate complex can polarize determines its reactivity. The potential energy barrier at A must be small because of the rapid exothermic transition to the triplet biradical intermediate at B. The "open" biradical intermediate is required to explain the formation of the carbonyl compounds (aldehydes and ketones) as well as the orientation of addition and non-stereospecificity of the  $O(^3P)$ -olefin reaction.

Biradical intermediates have also been proposed for the addition of triplet methylene to olefins.. Skell (16) reasoned that triplet methylene attacking a singlet ground state ethylene could not produce a cyclopropane molecule in a concerted manner, but in order for spin to be conserved, must form a triplet trimethylene intermediate. Rotation about a C-C bond in the intermediate would compete favorably with spin inversion and thus account for non-stereospecific addition. Hoffmann (99), from extended Huckel M.O. calculations, has shown that the potential energy surface for the reaction of triplet methylene with ethylene also indicates that a trimethylene intermediate, in which there are no barriers to rotation, is formed.

Bell (106), on the other hand, visualizes the reaction of triplet methylene with a double bond as the formation of an "incipient" cyclopropane ring that is equivalent to the



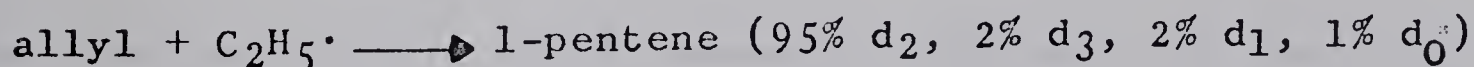
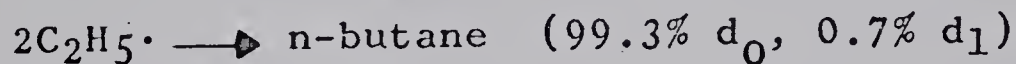
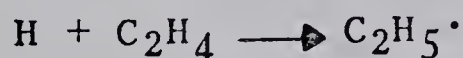


formation of a cyclopropane triplet species. The triplet intermediate can be considered to be a resonance hybrid of valence-bond structures:



Any one of the three C-C bonds in the incipient cyclopropane ring can open when the intermediate rearranges to acyclic isomers.

However, a recent investigation (87) of the triplet  $\text{CD}_2$  and ethylene reaction has shown that a "hot" cyclopropane species, in which the three C atoms are indistinguishable, is not an intermediate. The triplet  $\text{CD}_2$  was obtained from the mercury sensitization of  $\text{CD}_2\text{CO}$  and the isotopic distribution in the products arising from decomposition of the reaction intermediate indicated that trimethylene is the probable intermediate:



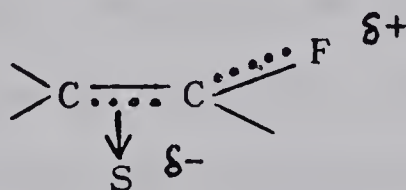
Elimination of H in the intermediate is expected to occur from the central carbon atom to form the stable allyl radical.





If an intermediate was formed in which the C atoms are indistinguishable, elimination of D atoms would occur and appreciably larger amounts of n-butane containing 1 and 2 deuterium atoms would be expected.

Application of the representation of the potential energy diagram (Fig. 17) to the  $S(^3P)$ -olefin reactions, would suggest that the activation energy of addition to the fluorinated ethylene systems will be smaller than that of addition to ethylene. The lower electron density in the double bond of the fluorinated ethylenes should result in a lowering of the contour of the repulsive potentials and thus lower the activation energy of the addition process. Resonance interactions in the charge-transfer complex should also decrease the slope of the attraction curve and lead to a further reduction in the activation energy of addition. Resonance stabilization of the intermediates would arise from ionic structures like those proposed to account for the lowering of the ionization potentials of the fluorinated ethylenes (94):



The results in Table XLVII, however, show that the activation energies for addition to the fluorinated ethylenes are larger. This may indicate that the potential energy barrier for the



addition reaction is not associated with the formation of a  $\pi$ -complex for the fluorinated ethylenes.

Furthermore, the structure of the biradical intermediate for S( $^3P$ ) atom addition to olefins must be modified to take into account the stereospecificity of the 2-butene (69), 1,2-dichloroethylene (70) and 1,2-difluoroethylene (Tables XXIX and XXX) reactions. It has been suggested (108) that spin interactions between the two unpaired electrons or with the vacant d orbital of the S atom in the intermediate, leads to the formation of an incipient  $\pi$ -molecular orbital. This would prevent free rotation about the C-C bond and lead to a stereospecific addition process. Such an intermediate in S-atom systems would also account for the absence of products arising from hydrogen migration in the activated complex, in contrast to triplet methylene and oxygen atom reactions with olefins.

The intermediate, which has been described as " $\pi$ -thiacyclopropane", was the suggested transition complex involved in the pyrolysis of episulfides (114). When ethylene episulfide was pyrolyzed, the only products obtained were ethylene and sulfur at temperatures up to 300°C. Since the activation energy for decomposition was found to be 12 kcal./mole less than the C-S bond dissociation energy, it was concluded that the rate determining step in pyrolysis of ethylene episulfide was not ring opening to give a freely rotating intermediate biradical. Further evidence was obtained from the pyrolysis





of cis-2-butene episulfide: cis-2-butene and sulfur were the only reaction products and there was no isomerization in the starting material, indicating that there is no rotation about the C-C bond in the intermediate.

Addition of 1-pentene to the ethylene episulfide system suppressed the rate of decomposition, but no new products were formed. Hence it was suggested that the formation of the olefin must result from a bimolecular reaction between the " $\pi$ -thiacyclopropane" complex and a substrate episulfide molecule. High energy photolysis of ethylene episulfide (97), on the other hand, may result in the formation of a thiodimethylene intermediate since addition reactions were observed with olefins.

Szwarc (109) has shown that while the activation energies for addition of the electrophilic species  $\text{CF}_3$  to a series of methylated ethylenes were linear with the ionization potential of the olefin, no correlation was found with the logarithms of the relative rate constants. From temperature studies of the  $\text{CF}_3$  addition reactions, propylene and isobutylene were found to have relative pre-exponential factors of approximately one, while those for cis and trans-2-butene were smaller by a factor of about five. The decrease in entropy of activation of the  $\alpha,\beta$ -methyl substituted olefins was attributed to restricted rotation around the incipient  $\text{C}^{\cdots}\text{CF}_3$  bond in the transition state. Since the entropy of activation depended on the location of the substituents, whereas the ionization



potentials and activation energies depended only on the number of substituents, it was concluded that the activated complex must resemble a radical adduct or  $\sigma$ -complex. The O-atom addition reaction would not be subject to hindered rotation in the transition state and it was suggested that arguments based on changes in activation energies alone may be incorrectly interpreted to favor the  $\pi$ -type transition-state.

In an earlier paper (110) it was suggested that for the addition reaction of  $\text{CF}_3$  to olefins, the attraction curve of Fig. 17 can be represented by a potential energy curve in which the electrons of the  $\pi$ -orbital are localized on the C-atoms of the double bond. For a series of substrates which have the same type of reaction center, such as  $=\text{CH}_2$  for a set of olefins having a terminal carbon atom, the repulsive curve will be unchanged since the charge density and rearrangement of atoms at the reaction center remains constant. Since the relative A factors remain constant for addition to such a series of reactants, the differences in activation energies will be proportional to the respective differences in atom localization energies. Hence a linear relationship between the relative reactivity and atom localization energy was found for  $\text{CF}_3$  addition to a series of unsubstituted aromatic hydrocarbons. These results were taken to indicate that an incipient C- $\text{CF}_3$  bond is formed in the transition state, which will resemble a  $\sigma$ -complex.





Fig. 18 shows that a similar relationship, for a series of olefins having the same reaction center, is obtained with the results from the  $S(^3P)$ -olefin addition reaction. The values for the atom localization energies were taken from reference 112. Although the data may be taken to indicate that the transition state resembles a  $\sigma$ -complex, these experimental results do not provide unequivocal evidence, since the question of  $\pi$ - or  $\sigma$ -complex intermediates in electrophilic addition reactions has not yet been resolved. The interpretations of Szwarc and Cvetanovic are highly simplified and must remain qualitative at best.

It is quite probable that mono- and biradical species add to the double bond via different reaction paths and therefore it may be unjustified to compare the reactivity of  $CF_3$  with that of S- or O-atoms. Even within the same periodic group the reactive intermediates may be different, since  $O(^3P)$  adds non-stereospecifically in contrast to  $S(^3P)$  atoms. In S-atom reactions, the barrier to rotation may be due to spin interaction of the unpaired electrons of the biradical intermediate, which is not really a  $\sigma$ -complex, but is perhaps better described as a  $\pi$ -complex since there is bonding to both C-atoms.



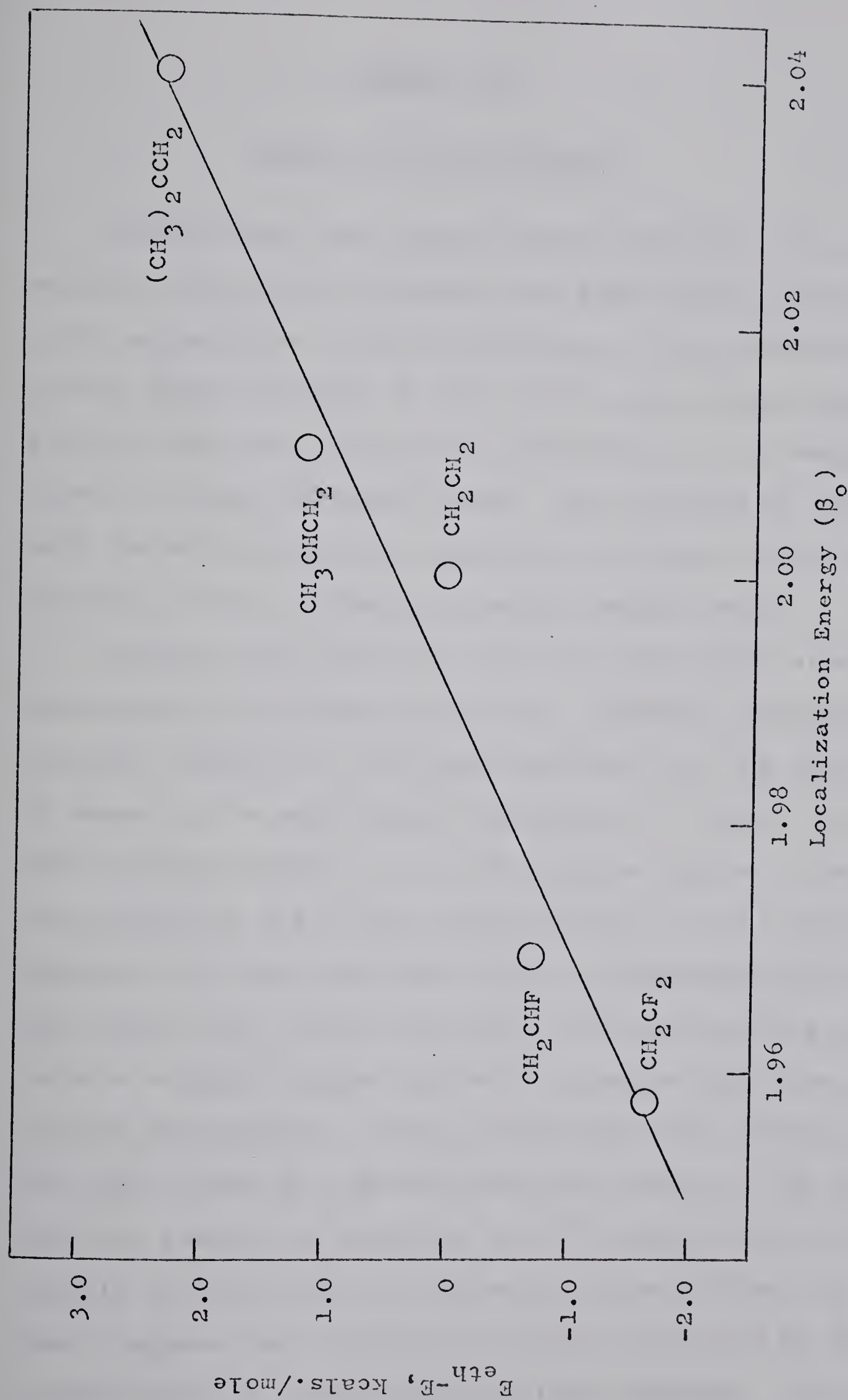


Fig. 18 Localization Energy vs.  $E_{eth} - E$  for a series of olefins having the same reaction center.



## CHAPTER VII

### SUMMARY AND CONCLUSIONS

Sulfur atoms from the gas phase photolysis of carbonyl sulfide react with hydrocarbon and fluorinated olefins to yield episulfides, vinylic mercaptans, if an unsubstituted carbon atom is present in the olefin, and alkenyl mercaptans if the olefin has alkyl group substituents. C-F bonds are inert to attack by sulfur atoms. The reaction of sulfur atoms with tetrafluoroethylene resulted in polymerization of the substrate with no volatile products being formed.

Studies with added  $\text{CO}_2$  indicated that  $\text{S}(^1\text{D})$  atoms are precursors for mercaptan formation. Alkenyl mercaptans are probably formed by  $\text{S}(^1\text{D})$  atom insertion into C-H bonds. This is shown by the statistical formation of 1-butene-3-thiol and 1-butene-4-thiol in the COS-1-butene system. The vinylic mercaptans may arise from isomerization of "hot" episulfide molecules or insertion into vinylic carbon-hydrogen bonds. The alkenyl and vinylic mercaptan forming-reactions were shown to have slightly larger activation energies than the episulfide forming-step. This may indicate that vinylic mercaptans are formed by a direct insertion process. The absence of products indicating insertion of  $\text{S}(^1\text{D})$  atoms into non-terminal vinylic C-H bonds of  $\alpha$  or  $\alpha,\beta$  substituted olefins, on the other hand, suggest that vinylic mercaptans are formed by the isomerization of energized episulfide molecules. The increased





degrees of freedom in these olefins may be sufficient to stabilize the "hot" episulfide molecules. The absence of a deuterium isotope effect showed that bond extension is not important in the transition complex for the formation of vinylic mercaptans. This is consistent with either mechanism as the mode of formation of vinylic mercaptans.

Triplet state sulfur atoms are inert towards C-H bonds, but add across double bonds to form episulfides. The addition to the 1,2-difluoroethylenes is stereospecific and may arise from an increased barrier to rotation in the initially formed biradical. The rotational barrier may be due to spin interaction of the unpaired electrons of the biradical.

An increase in the ratio (mercaptan)/(episulfide) with increasing energy of photolysis was attributed to excess translational energy carried by the sulfur atom.

The addition of CO to the  $\text{COS-C}_2\text{H}_4$  system indicated that no reaction, other than electronic deactivation, occurs between  $\text{S}(^1\text{D})$  atoms and CO. Xenon is inert towards attack by  $\text{S}(^1\text{D})$  atoms and is ineffective in electronic deactivation.

The relative rates of  $\text{S}(^3\text{P})$  atom addition to fluorinated ethylenes did not correlate with the ionization potential of the olefin as was observed for hydrocarbon olefins. However, a linear correlation was found with the atom localization energies of the fluorinated olefins. It does not necessarily follow that the transition state resembles a  $\sigma$ -complex, since stereospecific addition of  $\text{S}(^3\text{P})$  atoms to



olefins suggests bonding to both carbon atoms of the double bond. Such an intermediate is perhaps better described as a  $\pi$ -complex.



## APPENDIX A

### Mass Spectral Data

The following mass spectra were obtained  
on a Metropolitan Vickers Model MS-2 mass spectrometer  
operated at 70 eV.





MS-1: Vinyl Mercaptan

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
25	3.8	46	3.1
26	14.0	47	6.1
27	42.7	56	6.7
28	8.4	57	25.0
29	9.5	58	41.8
32	8.8	59	92.3
33	8.7	60	<u>100</u>
34	20.7	61	8.0
44	6.3	62	10.7
45	73.2		

MS-2: Ethylene Episulfide

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
25	2.1	46	5.0
26	9.7	47	4.2
27	24.2	56	2.7
28	6.2	57	11.3
29	2.3	58	25.5
32	6.6	59	74.7
33	3.2	60	<u>100</u>
34	9.8	61	6.3
44	4.7	62	4.3
45	88.2		

MS-3: Trans-Propene-1-Thiol

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
15	1.6	39	55.0	58	6.9
26	2.8	40	6.4	59	13.7
27	6.1	41	<u>100</u>	68	2.2
29	2.4	42	5.0	69	7.4
33	2.5	43	1.5	71	9.3
34	3.9	45	73.0	72	1.9
35	3.4	46	23.0	73	14.1
36	0.9	47	16.8	74	81.6
37	4.8	48	2.1	75	4.6
38	6.8	57	3.5	76	5.4



MS-4: Cis-Propene-1-Thiol

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
15	1.8	39	57.0	58	7.1
26	3.2	40	6.6	59	13.7
27	7.1	41	<u>100</u>	68	2.2
29	2.8	42	5.3	69	8.4
33	2.8	43	1.7	71	9.1
34	4.5	45	74.5	72	2.2
35	3.6	46	23.2	73	14.8
36	1.4	47	19.6	74	84.2
37	5.0	48	2.2	75	4.7
38	7.1	57	3.8	76	6.0

MS-5: Allyl Mercaptan

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
15	2.7	39	72.5	58	3.6
26	4.0	40	8.5	59	8.2
27	10.9	41	97.8	68	1.5
29	3.9	42	6.9	69	5.1
33	4.2	43	6.2	71	4.8
34	3.3	45	40.6	72	1.2
35	2.1	46	17.4	73	8.7
36	1.2	47	24.6	74	<u>100</u>
37	6.8	48	2.9	75	5.0
38	11.1	57	3.3	76	8.3

MS-6: Propylene Episulfide

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
15	2.6	38	6.4	57	4.2
26	5.5	39	41.7	58	9.8
27	12.4	40	6.2	59	33.4
29	2.3	41	<u>100</u>	69	3.0
33	1.8	43	2.9	71	3.9
34	2.0	45	56.2	73	10.8
35	1.7	46	50.0	74	99.9
36	1.0	47	14.0	75	4.5
37	4.0	48	3.6	76	6.2



MS-7: 2-Methylpropene-1-Thiol

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
26	3.2	47	25.0	60	20.0
27	30.3	48	4.7	61	3.2
29	36.6	49	2.7	67	7.4
34	2.8	50	6.0	68	7.2
36	3.4	51	7.1	69	8.1
37	3.4	52	2.4	71	5.6
38	7.3	53	36.5	73	28.7
39	62.5	54	30.0	81	3.1
40	5.7	55	100	85	5.5
41	37.2	56	7.0	87	4.7
43	9.8	57	3.0	88	98.0
45	68.1	58	6.2	89	5.5
46	12.3	59	20.6	90	4.6

MS-8: Trans-1-Butene-1-Thiol

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
26	6.0	46	8.2	69	5.9
27	37.9	47	25.1	71	2.8
29	47.5	49	2.3	73	11.9
33	3.3	51	6.5	74	1.0
34	5.5	53	10.1	74	1.0
38	3.8	54	20.9	76	1.9
39	42.0	55	100	81	3.1
40	3.5	56	9.6	83	1.4
41	20.4	57	11.6	85	2.6
42	3.1	58	6.1	87	1.1
43	7.8	59	9.9	88	39.4
44	2.9	60	11.0	89	2.3
45	37.0	61	1.6	90	2.2

MS-9: Cis-1-Butene-1-Thiol

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
26	6.3	46	13.9	69	5.6
27	30.3	47	31.5	71	7.4
29	33.9	49	2.7	73	50.4
33	4.5	51	6.4	74	2.5
34	7.9	53	20.2	75	2.5
38	5.4	54	27.0	76	3.0
39	44.9	55	100	81	2.2
40	3.0	56	7.5	85	6.2
41	16.8	57	7.9	87	3.6
42	3.2	58	13.4	88	68.0
43	6.2	59	17.7	89	4.2
44	6.2	60	25.6	90	3.5
45	98.5	61	2.8		





MS-10: Trans-2-Fluoroethene-1-Thiol

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
26	7.0	58	21.6
27	8.6	59	9.4
31	4.5	60	4.1
33	17.0	63	2.0
34	5.3	76	10.8
44	7.3	77	18.1
45	<u>100</u>	78	85.5
46	8.3	79	2.6
47	22.6	80	3.2
57	17.2		

MS-11: Cis-2-Fluoroethene-1-Thiol

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
26	4.7	58	20.2
27	1.6	59	7.8
31	3.8	60	1.4
33	16.6	63	2.0
34	4.5	76	8.8
44	6.6	77	15.5
45	<u>100</u>	78	75.5
46	3.8	79	2.9
47	6.0	80	3.4
57	14.9		

MS-12: Fluoroethylene Episulfide

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
26	7.0	58	20.2
27	2.3	59	7.8
31	2.5	60	1.4
33	6.8	63	3.7
34	2.1	76	3.1
44	4.3	77	4.9
45	<u>100</u>	78	67.5
46	8.5	79	2.3
47	5.5	80	3.0
57	8.8		



MS-13: 2,2-Difluorovinyl Mercaptan

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
31	10.6	57	5.6
32	6.7	58	1.2
33	9.8	59	0.7
34	1.2	60	1.0
44	10.1	63	8.2
45	<u>100</u>	64	3.3
46	27.3	65	3.8
47	8.4	94	5.8
48	3.7	95	5.6
50	2.8	96	46.9
51	4.6	97	2.8
56	1.8	98	3.2

MS-14: 1,1-Difluoroethylene Episulfide

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
31	19.5	57	19.0
32	6.5	58	6.6
33	34.4	59	3.3
34	3.8	60	2.0
44	58.4	63	13.3
45	<u>100</u>	64	23.4
46	87.7	65	20.5
47	13.6	94	2.3
48	5.9	95	2.1
50	3.9	96	98.7
51	12.3	97	3.6
56	2.3	98	4.9

MS-15: Trans-1,2-Difluoroethylene Episulfide

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
25	0.8	57	9.4
26	2.6	58	3.1
31	12.9	63	75.0
32	12.3	64	5.3
33	35.8	65	5.5
34	1.3	76	23.5
38	1.0	77	24.2
44	6.9	78	2.0
45	92.7	95	1.2
46	3.3	96	<u>100</u>
47	4.4	97	2.9
51	3.5	98	4.3
56	1.0		



MS-16: Cis-1,2-Difluoroethylene Episulfide

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
25	1.5	57	13.9
26	2.9	58	3.9
31	12.5	63	82.3
32	14.5	64	11.7
33	35.7	65	8.2
34	1.3	76	27.0
38	1.0	77	11.3
44	8.0	78	1.8
45	<u>100</u>	95	1.8
46	3.3	96	99.3
47	4.4	97	3.0
51	3.9	98	4.6
56	2.1		

MS-17: Trifluoroethylene Episulfide

<u>m/e</u>	<u>Rel. Int.</u>	<u>m/e</u>	<u>Rel. Int.</u>
31	15.7	66	2.0
32	10.7	69	1.3
44	4.9	76	1.1
45	<u>100</u>	82	6.5
46	2.3	94	3.6
47	5.3	95	4.4
50	2.5	113	0.7
51	16.1	114	22.6
63	25.3	115	0.8
64	46.9	116	1.1
65	1.9		



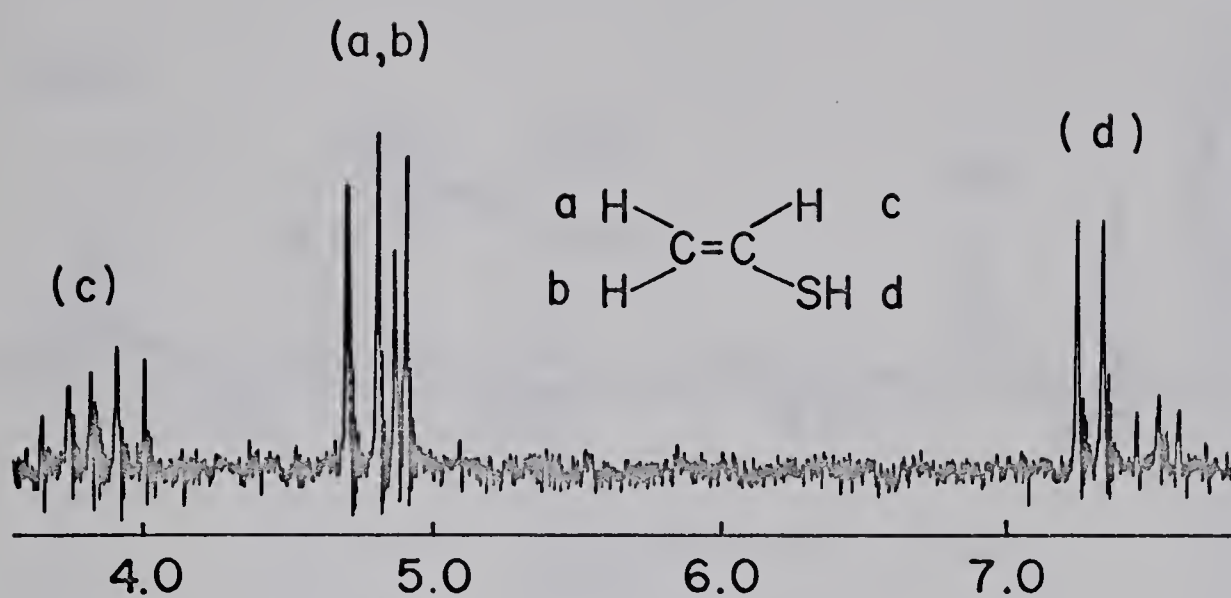
## APPENDIX B

## N.M.R. Spectra

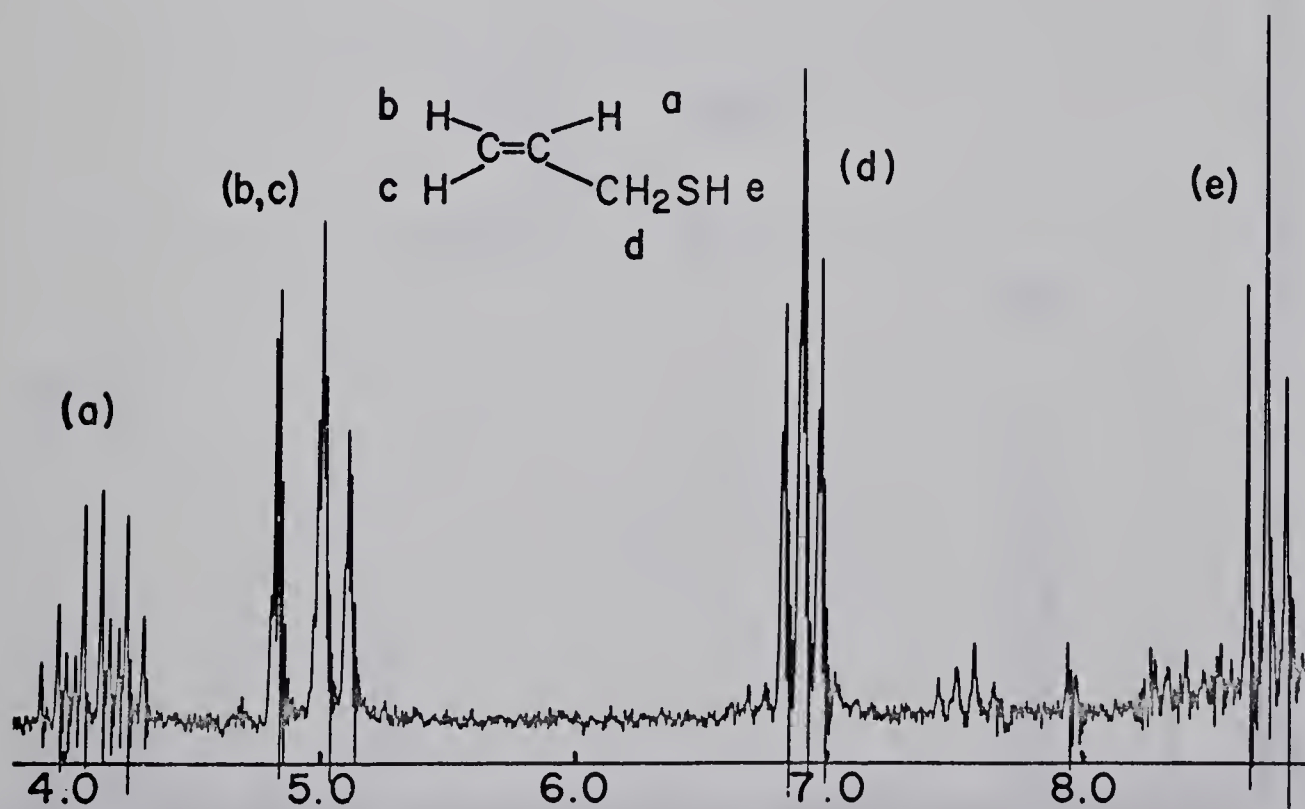
The following N.M.R. spectra were obtained  
on a Varian 100 Mc spectrometer.





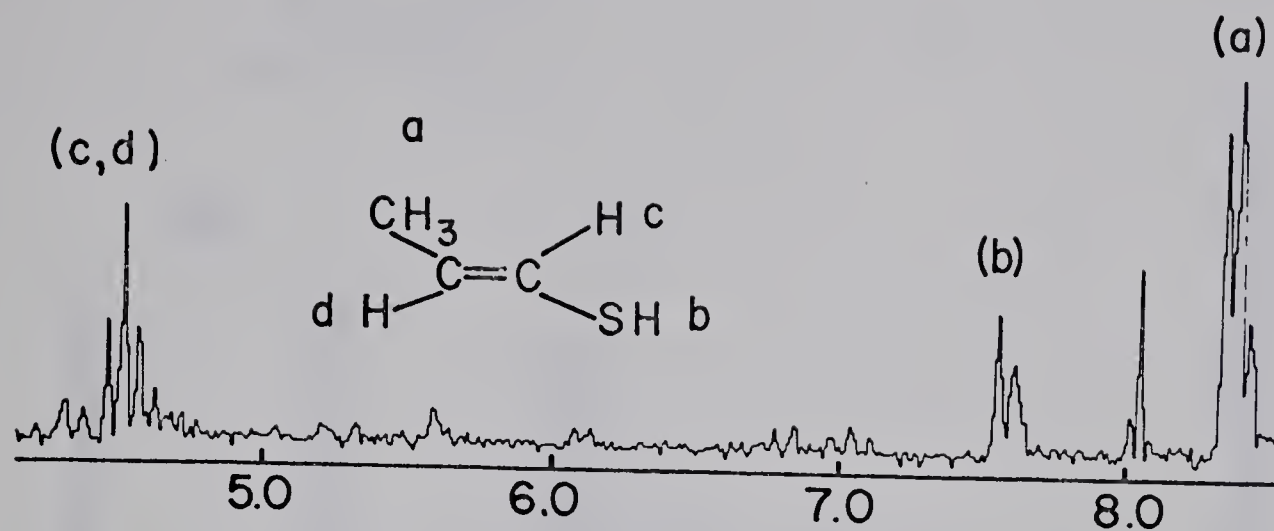
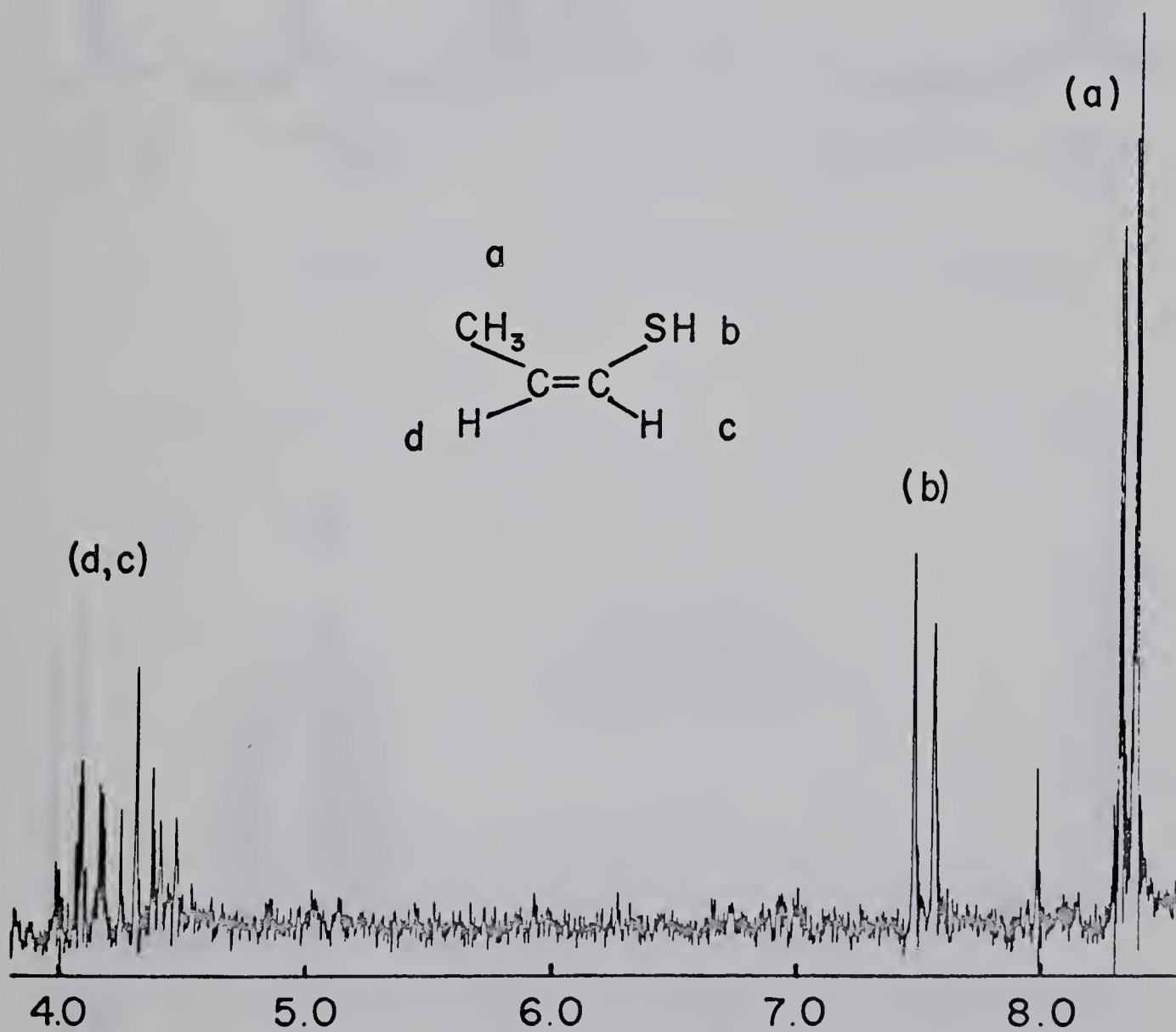


N.M.R.-1: Vinyl Mercaptan

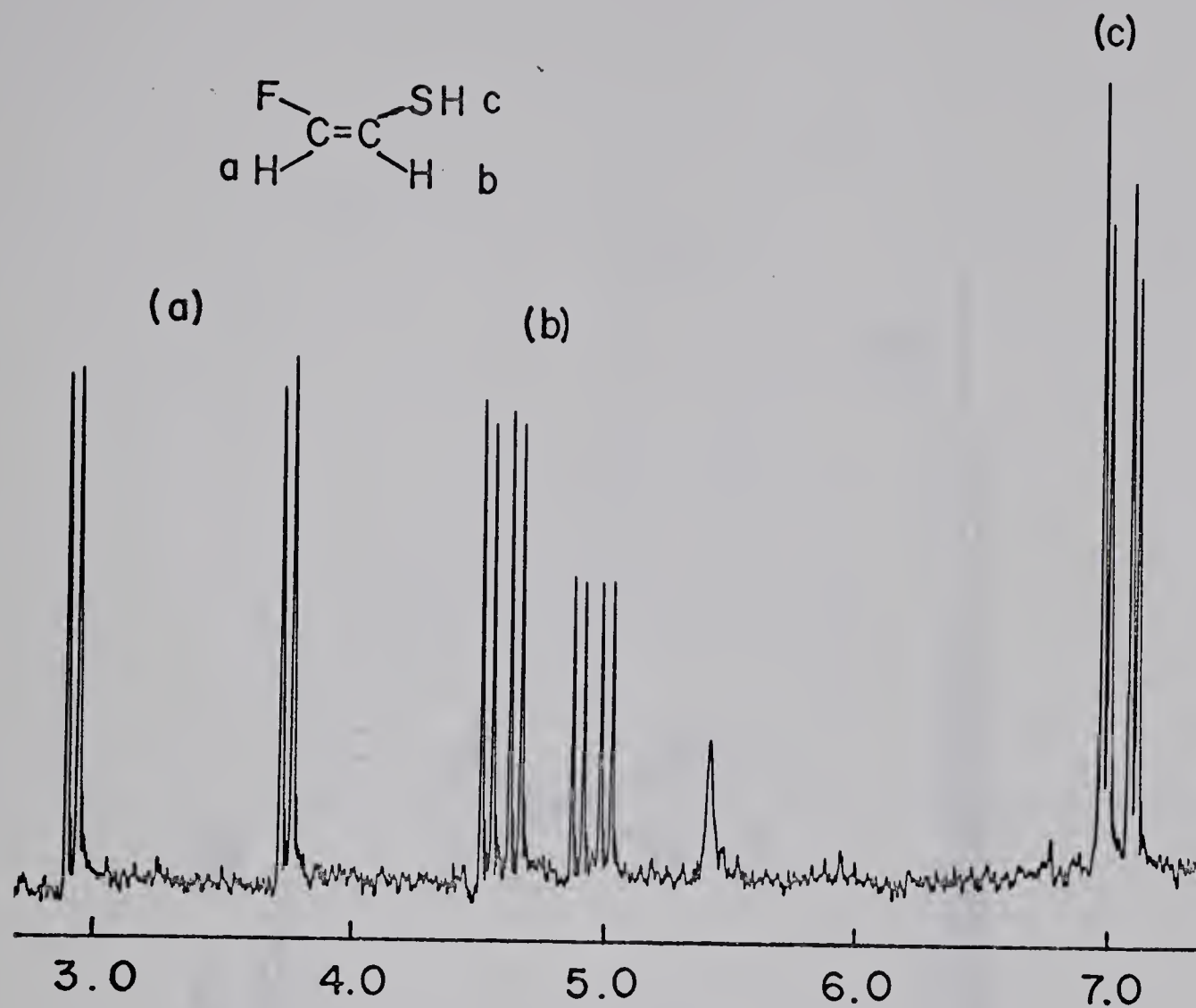


N.M.R.-2: Allyl Mercaptan

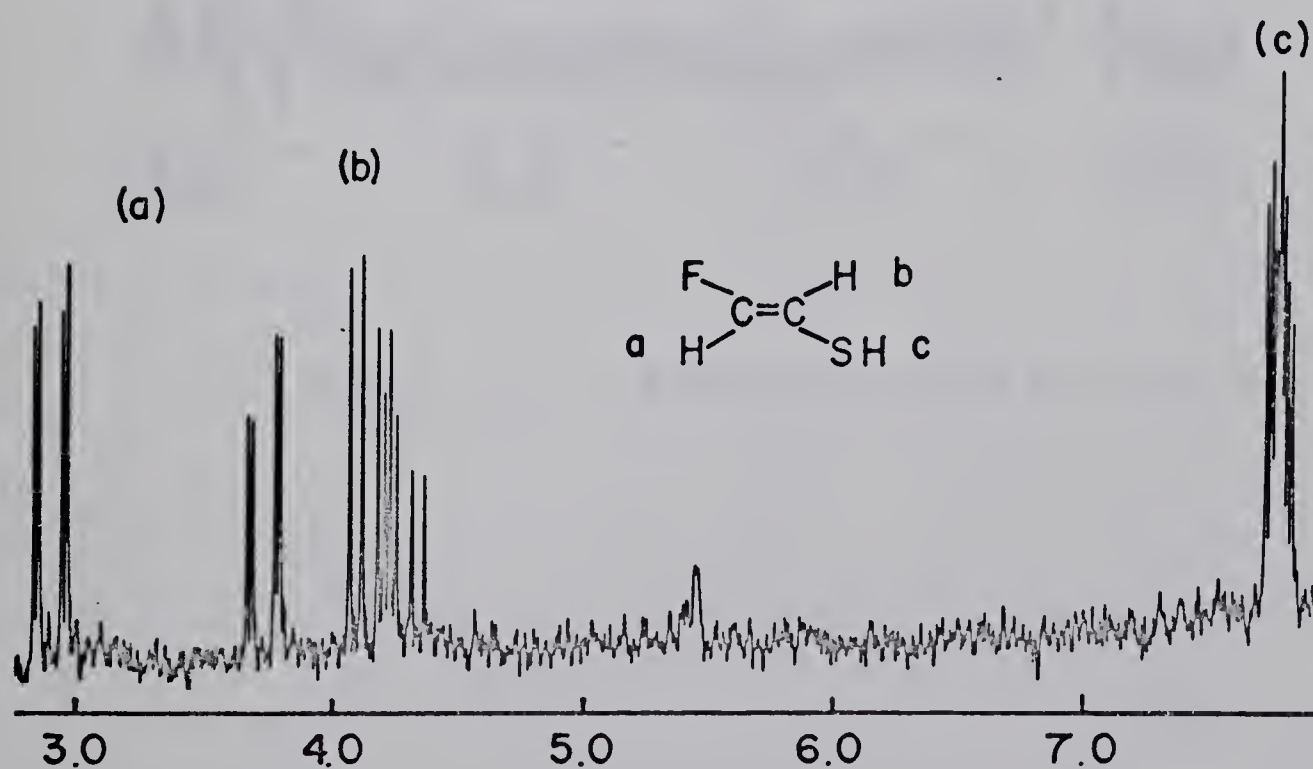


N.M.R.-3: trans-Propene-1-ThiolN.M.R.-4: cis-Propene-1-Thiol





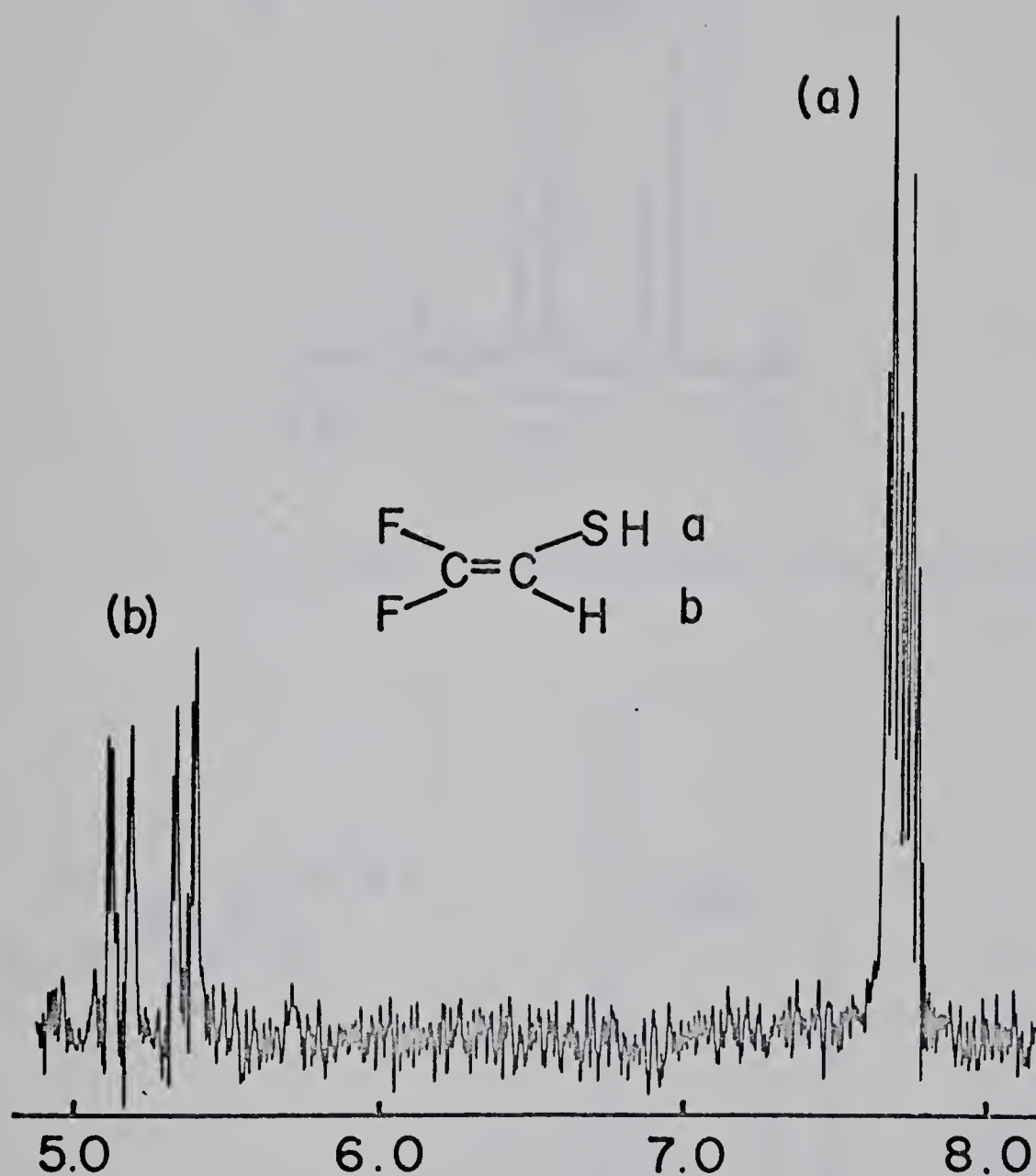
N.M.R.-5: cis-2-Fluoroethene-1-Thiol



N.M.R.-6: trans-2-Fluoroethene-1-Thiol

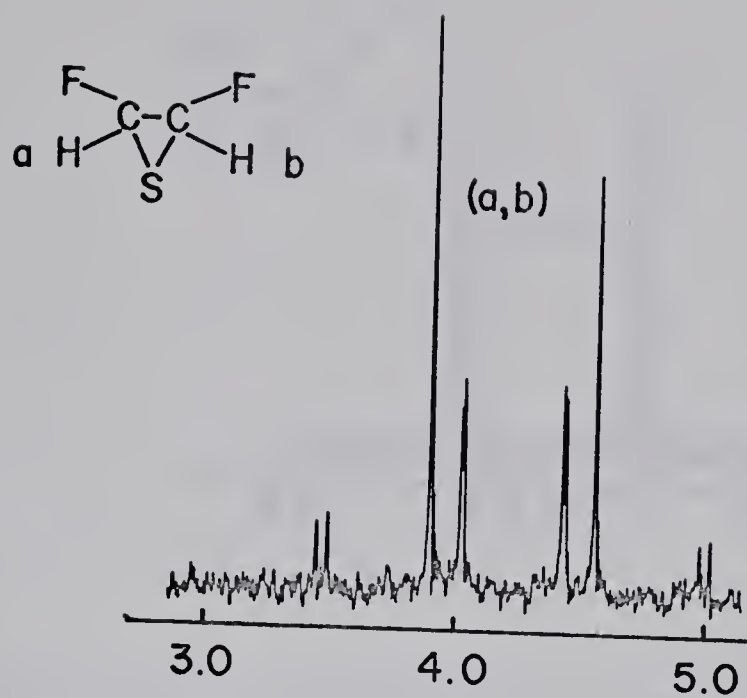




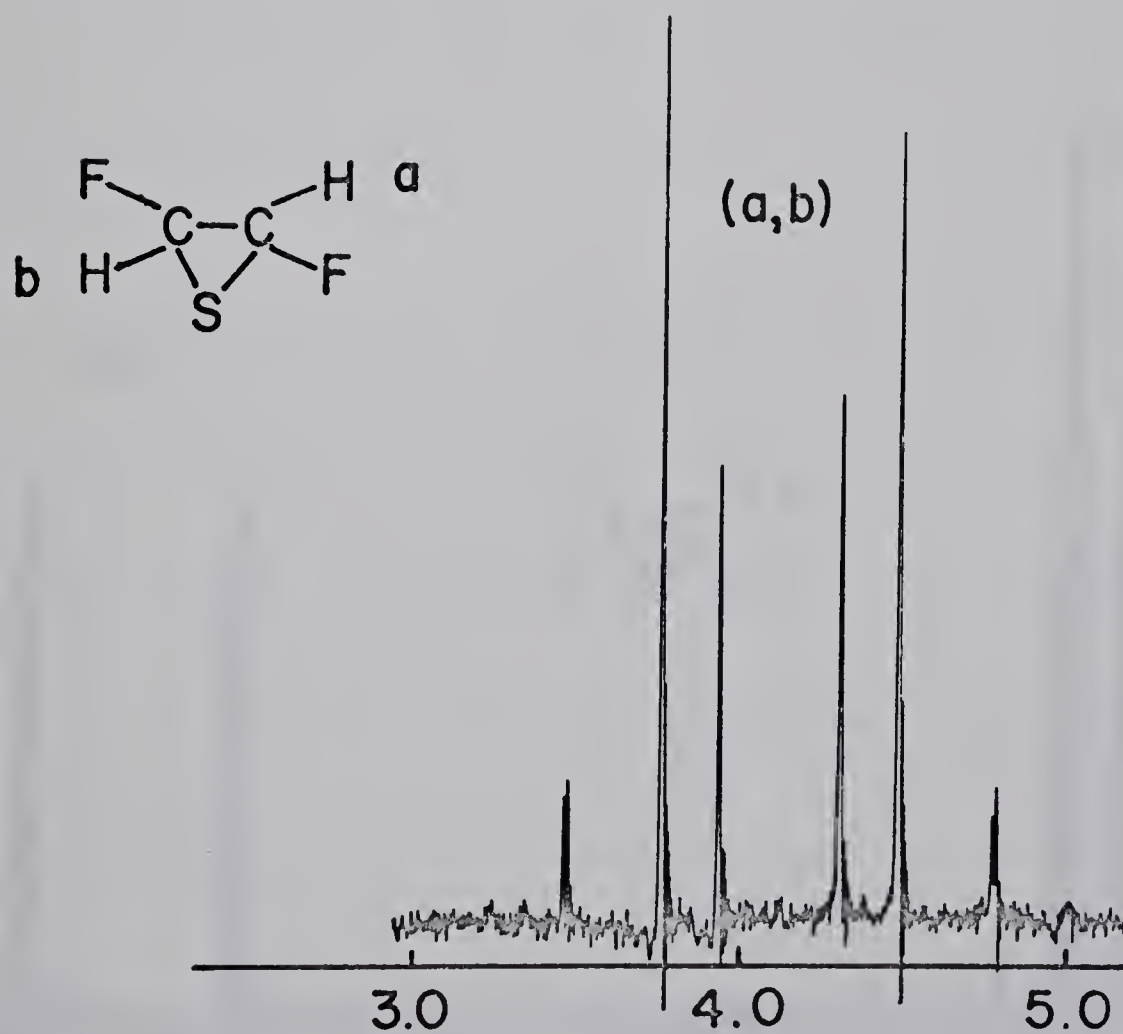


N.M.R.-7: 2,2-Difluorovinyl Mercaptan



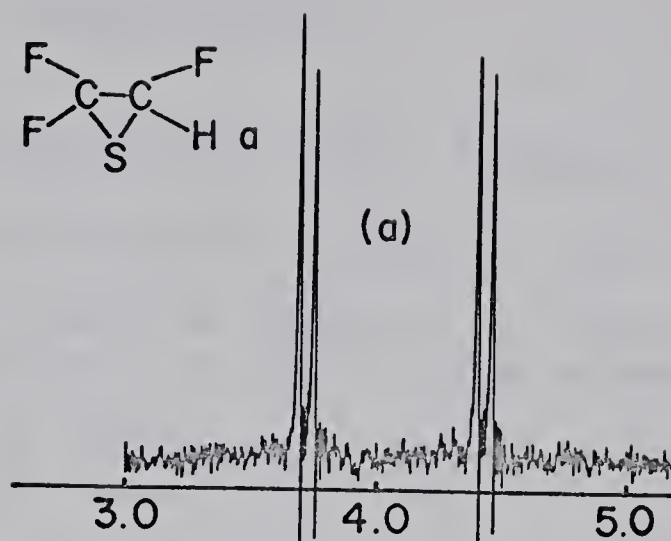


N.M.R.-8: cis-1,2-Difluoroethylene Episulfide

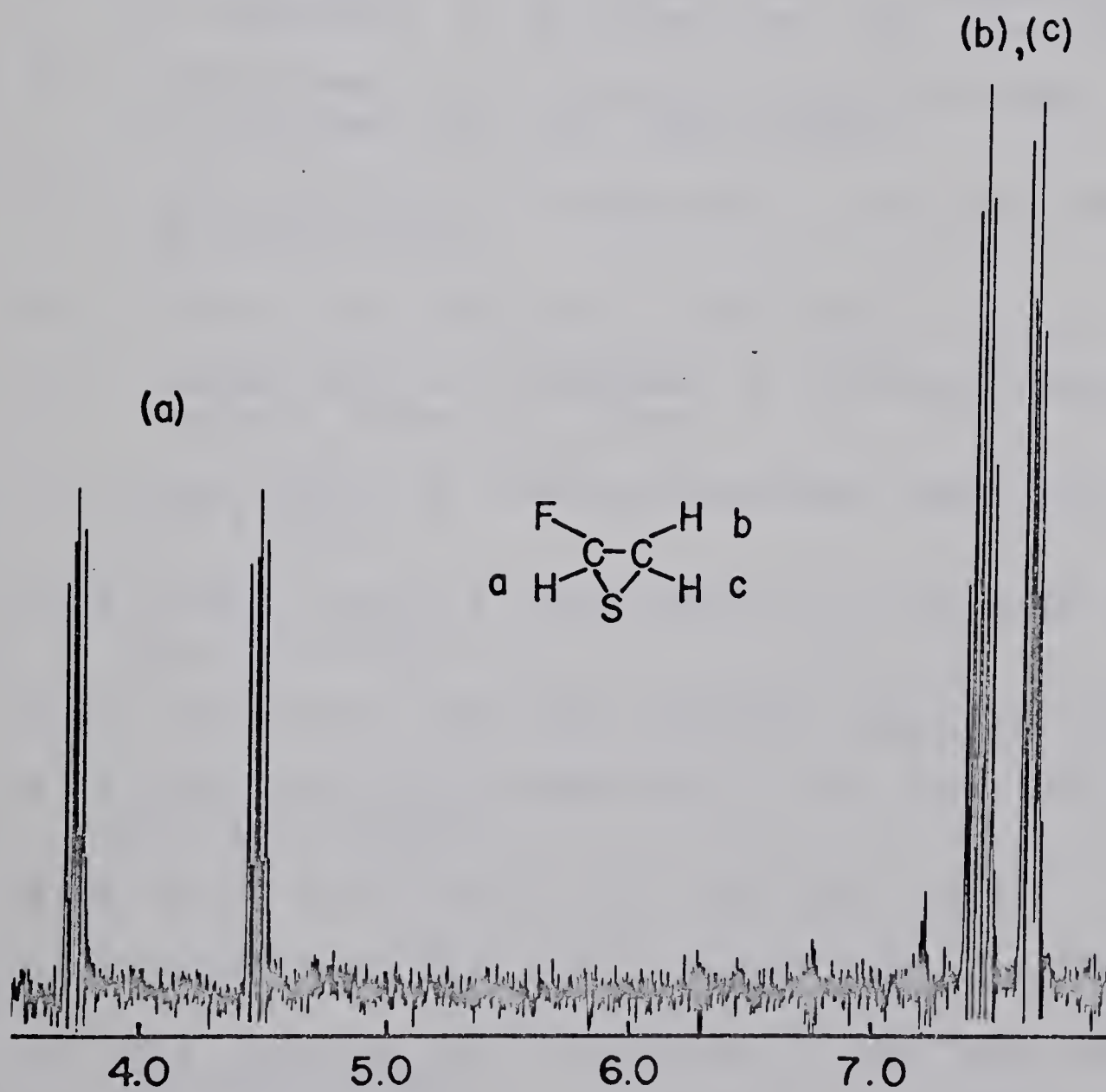


N.M.R.-9: trans-1,2-Difluoroethylene Episulfide





N.M.R.-10: Trifluoroethylene Episulfide



N.M.R.-11: Fluoroethylene Episulfide



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